THE INTERLAYER FORMED BETWEEN IRON AND AN ACRYLIC LATEX.

A Thesis Submitted to the University of Surrey for the Degree of Doctor of Philosophy.

by

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ABSTRACT

The anti-corrosive nature of steels coated with a commercially available acidic water-borne latex primer has been demonstrated to be considerably enhanced by the formation of an interfacial film between the coating and metal substrate. Novel sample preparation has enabled microtomed cross-sections of latex polymer coated metals to be analysed by TEM to establish the morphology and structure of the interlayer. Combined EDX and electron diffraction presents evidence for a chlorine containing mixed valence iron oxide/hydroxide – a pyroaurite-type compound, green rust I – existing in this region and attributes this formation to the observed enhanced anti-corrosive properties.

Modifications to the latex polymer by soluble ionic pigment additions was performed to attempt to enhance the anti-corrosive nature of the coating by formation of different pyroaurite-type compounds based on the formula $\text{Mg}_6\text{Fe}_2(\text{OH})_16\text{CO}_3\cdot4\text{H}_2\text{O}$, where Mg may be substituted by a suitable divalent cation and likewise Fe substituted by a suitable trivalent cation. Analysis of these modified coatings by TEM, XPS and A.C. impedance spectroscopy has elucidated their anti-corrosive action and identified the presence of polymer/metal and polymer/air films formed by ionic additions. In particular, the ionic addition of Mg(II) is found to considerably increase corrosion resistance in these latex coatings immersed in 3% NaCl.

Models are presented for green rust formation and corrosion protection enhancement by soluble ionic additions.
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1 INTRODUCTION

1.1. Corrosion of Mild Steel

The wider definition of corrosion as 'the destruction of a substance or its properties because of a reaction with its environment' (1) is realised in the case of most metals by their reaction with oxygen to the thermodynamically more favourable oxide state. Figure 1 shows schematically the corrosion of mild steel in the presence of water, giving particular emphasis to the electrochemical reactions required for corrosion to occur. It is necessary to consider the individual elements of this corrosion process, since corrosion is a combination of processes, any one of which may be rate controlling.

The essential elements of corrosion (w.r.t. Fig. 1) are thus:-

a) the anode, where dissolution of the bulk metal occurs and electrons are produced.

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^{-}
\]

b) the cathode, where electrons are consumed by reduction of solute species to counter the anodic reaction by either

\[
2H^+ + 2e^- \rightarrow H_2
\]
\[
2H + \frac{1}{2}O_2 \rightarrow H_2O
\]
\[
2H_2O + O_2 + 4e^- \rightarrow 4OH^-
\]

c) the electrolyte provides a medium by which passage of ions (i.e. H\(^+\) and OH\(^-\)) can occur thus sustaining corrosion.
Figure 1 Electrochemical aqueous corrosion of mild steel. (After (68)).
d) the external circuit, generally the metal itself when the anodic and cathodic sites are on the metal surface, provides the final contact for the electrochemical processes to take place, by allowing electron flow between anode and cathode.

Aqueous corrosion thus occurs when three reagents are present; oxygen, water and electrolytic ions. There will be no corrosion unless all three are present at the corrosion site, and a potential difference is activated. It therefore becomes clear that the restriction of any elemental step or process will lead directly to the reduction in corrosion. The manner in which organic coatings can do this will therefore be discussed.

1.2. Corrosion Protection by Organic Coatings

An organic coating was originally applied to a metal substrate in order to present a physical barrier between a metal and an aggressive environment. However, it is now generally accepted that such coatings are, in fact, permeable to both water and oxygen (2) and merely act to retard the passage of these species in order to suppress corrosion. The rate of passage of these penetrants will depend on many factors; the availability at the coating surface, their solubility in the coating, their diffusivity through the coating, their affinity for any pigment particles present and their rate of consumption at the corrosion site. Realising that the elimination of the cathodic reaction is not a realistic possibility in most systems, we must consider other transport processes as possible rate controlling steps. In particular, it is found that the movement of charged ions between
the anodic and cathodic sites, which are often well separated, is the rate controlling step in corrosion of organic coated metals. This may be explained simply by the fact that whereas the metal, being a conductor, allows the passage of electrons very easily, the migration of ions towards or from the metal surface must occur through the polymer coating, generally of high electrolytic resistance. This is generally referred to as resistance inhibition. Furthermore, an electrical double layer consisting of an inner layer of oriented water dipoles next to the electrode surface and an outer layer of solvated ions in solution (outer Helmholtz plane) provides additional resistance to electron flow at the cathode. This polarisation of the anode-cathode reaction by charge transfer kinetics and its effect on substrate corrosion was demonstrated by Mayne (3,4) who identified two distinct modes of conduction in polymer films. When polymer films were detached from substrates and tested in KCl solutions it was found that the conductivity of the films ran either counter to the conductivity of the test solution or followed it. These areas were subsequently designated D type, for direct conduction, or I type for inverse behaviour. It has hence been shown that underfilm corrosion occurs in D type areas where the resistivity of the polymer film is impaired in some way.

Mayne was also able to show that for paint films studied, both D and I type regions were present, probably due to the random nature of the crosslinking process producing differing cross-linked polymer densities. It is, therefore, usual for organic coatings to have pigment additions in a paint formulation to give a further degree of corrosion inhibition. The formulation
of paints will be discussed later.

The basis for an organic coating to give good protection to a metal substrate on film forming properties alone can thus be summarised as:-

1) low permeability to oxygen and water
2) high electrolytic resistance

1.3 Basic Paint Formulation

Paint formulations vary depending on end use, yet possess general characteristics which may be conveniently classified into the following categories:

a) Binder:- generally a polymer or monomer dispersed in a solvent. On evaporation of the solvent (or activation of the monomer), polymerisation and coalescence occurs to form a continuous film over the substrate.

b) Pigment additions:- additions to provide colour, corrosion inhibition and adhesion between paint layers.

c) Specific additives:- i.e to control paint stability, fungicides, flame retardants etc.

Paints formulated to protect metals (primers) can again be divided into three main areas:

a) Barrier primers:- these primers provide a physical barrier to moisture, oxygen and ions, hence impede corrosion by artificially increasing the resistance of the corrosion cell. Pigment additions tend to be flake-like (i.e. mica, glass flake, micaceous iron oxide) which effectively increase the path length
for any species permeating the film.

b) Zinc rich primers:— these are highly loaded with metallic zinc (>80% by vol.) which corrodes sacrificially to protect the steel.

c) Inhibiting primers:— inhibitors act by retarding the electrochemical corrosion reactions on the metal surface. The traditionally used anti-corrosive pigments are red lead, zinc and strontium chromate and zinc phosphate. However, the use of these pigments is much in decline particularly on toxicity grounds. Legislation exists on the use of red lead in paints and hexavalent chromates are widely suspected of being carcinogenic. Zinc phosphate, on the other hand, is considered non-toxic but the variable nature of its protection has cast doubts within the industry of its effectiveness.

The formulation and development of HALOFLEX (a tradename registered to ICI plc), which is the subject of later study, will be discussed in terms of its ability to prevent corrosion.

1.4. Development of HALOFLEX as a Water-borne Coating

The basic necessity for a paint to form a continuous film over the substrate essentially dictates the use of organic materials as film formers in all but very special cases due to their ability to readily polymerise. The general rule for solubility that 'like dissolves like' regarding polar and non-polar solvents, holds true for most paint resins, in that non-polar hydrocarbons are generally soluble in non-polar solvents i.e. xylene, toluene etc., but not in water - a highly polar solvent. Polymers soluble
in water tend to be derived from highly polar monomers and include vinyl alcohols, acrylic acids and acrylonitriles. However, paints based on these polymers have shown poor protective properties due primarily to high permeability to water vapour and oxygen (5) but also because of flash and early rusting, drying properties, adhesion and rheology considerations (6). The desire for water-borne coatings in this respect would thus seem misguided. The impetus for these coatings, in fact, derives from a series of laws passed in the United States (7) designed to control the emission of solvent pollutants into the atmosphere. Europe, although not obviously bound by these laws, recognises the U.S. as the largest single market in the free world and coupled with the rising and erratic cost of oil based derivatives has sought to develop suitable alternatives.

ICI pinpointed the failings of the available water based emulsion polymers on two main factors (5);

a) choice of co-monomers in the emulsion failed to provide a barrier to the diffusion of water and oxygen.

b) polymerisation techniques involved high concentrations of surfactants which, by reaction with monomer, can form graft copolymers, impairing the particle coalescence in film formation, ultimately leading to a reduction in barrier properties of the final paint film.

The polymer designed by ICI to counter these deficiencies was based on existing chlorinated rubber technology; a latex which exhibits low permeability to oxygen and water as well as good resistance to a wide range of chemicals (8), but is also a solvent
(organic) borne polymer binder. The high chlorine content, to which the good barrier properties have been attributed (5), was achieved by copolymerising vinyl chloride and vinylidene chloride with additions of esters of acrylic acids to control film forming characteristics and to introduce thermal stability; vinyl polymers readily degrade when the degree of polymerisation is greater than approximately five (9).

This chlorine containing vinyl acrylic latex copolymer - Haloflex - when used in practical paint systems, has presented features not found in conventional latices. In particular is the tendency of the copolymer to dehydrochlorinate (degrade with the evolution of HCl) when exposed to alkaline conditions. It is for this reason that Haloflex is used in acidified paint formulations, with a final pH in the region of 4-5 when it is found that the increase in chloride ion concentration on storage is negligible. Pigment additions are chosen, which buffer the paint in this pH range, and other additives such as surfactants and thickeners are selected on the basis of their effectiveness in this pH range (10). The concept of a slightly acidic emulsion primer is new and the various developments necessary for its successful performance are covered in a series of patents (11, 12).

The primer formulations used in the studies of polymer/metal interactions are given in Appendix 1.

1.5. Properties and Uses of Haloflex-based Paints

Water-borne coatings are increasingly taking a larger share of the organic coatings market, replacing solvent-based coatings,
wherever feasible, due mainly to their 'environmental friendliness' (13, 14). Nicholson (15) has reviewed different classes and uses of such coatings and emphasises the major drawbacks of using water-borne coatings, namely water sensitivity, humidity affecting drying, poor wetting of substrate and flash rusting.

The paints based on Haloflex binders have been found to alleviate a number of these problems. Padget and Moreland (16) compared a number of commercial latex types measuring water permeability and ionic film resistance of free films and applied paints. Their results showed that the permeability of Haloflex films was approximately 100-fold lower than that of the other latex films tested. A.C. impedance tests on applied paints also demonstrated, by the theory of Brasher and Kingsbury (17), that water uptake into the paint film was far less than that for other paints. The prediction of greater anti-corrosive behaviour as a result of this reduced water sensitivity was supported by coating performance under a standard salt spray test (ASTM B117-75.) Further studies (18) on Haloflex paints not only demonstrated the excellent anti-corrosive performance of the coating but also revealed the presence of an interface reaction producing a protective film at the metal surface.

This interface reaction, evidenced by an underfilm darkening phenomena, was investigated by A.C. impedance and interfacial loss studies (16). Thus it seemed clear that the superior durability of this system, compared with other water-borne coatings, was due, at least in part, to an interfacial reaction leading to an extended interphase zone between substrate and coating. This interfacial
film was found to be protective and early characterisation studies by XRD suggested that it was possibly a member of the pyroaurite group of compounds characterised by the general formula

\[ M_xR_y(OH)_{2x} + 3y-2z (A^{2-})_z \cdot 2H_2O \]

where M is a divalent cation, R is a trivalent cation and A is an anion.

It is a study of the formation of this film in Haloflex paints which forms the basis of the work described in this report.

1.6. The Pyroaurite Class of Compounds

The naturally occurring mineral Pyroaurite, \( \text{Mg}_6\text{Fe}_2(\text{OH})_{16}\text{CO}_3.4\text{H}_2\text{O} \) forms hexagonal plate-like crystals exhibiting interesting structural features to both mineralogist and materials scientist alike. By introducing trivalent cations into a Brucite-like Me(II)(OH)_2 layer, a double hydroxide ionic structure \([\text{Me(II)}_{1-x} \text{Me(III)}_x(\text{OH})_2]^{x+}\) can be obtained (19). For electrical neutrality an addition of anions \( X^- \) is necessary to stabilise this ionic structure. This can be achieved by the formation of hydrogen bonds either directly with the anion or by involvement with an associated water molecule i.e. O-H..X or O-H-OH-H..X. These additional anions and water molecules are observed to form an interlayer between the mixed hydroxide layers, creating a double layer structure to the final compound. Allman (19) points out that this layer is so weakly bonded that the component atoms can display great mobility. Taylor (20) has also pointed out that some of these interlayer sites can also be empty thereby creating a means of accepting anions into empty sites or
allowing the possibility of anion exchange with molecules of the weakly bound interlayers under appropriate conditions.

The appearance of a corrosion product with a pyroaurite type structure has been cited in a number of cases as the cause of an unexpectedly low rate of corrosion observed on components in service. Austing et al. (21) identified a hydrotalcite scale \( \text{Mg}_{18}\text{Al}_6(\text{OH})_{48}(\text{CO}_3)_3\cdot12\text{H}_2\text{O} \) (a structure related to pyroaurite) as being present on the surface of aluminium heat exchangers used in desalination plants. An increased resistance to anodic breakdown of the corrosion film formed on the Al surface was attributed to the formation of this scale, whereby it is claimed that the scale exhibited a buffering action by varying the Mg:Al ratio in the hydrotalcite according to pH. Similar studies by (22) further demonstrated by XPS the buffering capacity of hydrotalcite films formed on aluminium brass condenser tubes in seaside power stations, wherein such tubes were found to exhibit enhanced corrosion resistance. Stampfl (23) also reported a green basic carbonate compound with a pyroaurite type structure, found in water mains pipes around Stuttgart and gave it a composition corresponding to: \( \text{Fe}^{2+}\text{Fe}^{3+}_2(\text{OH})_{12}\cdot\text{CO}_3\cdot3\text{H}_2\text{O} \). This latter formation arose due to the conditions of limited oxidation existing at the corroding interface, whereby deaerated aqueous media was insufficient to fully oxidise corroding iron at the anode to a trivalent state. Similar compounds have been found in domestic central heating systems and have been referred to as 'green rusts' (24). The corrosion of cast irons in such systems has been treated by McEnaney and Smith (24 - 26) where it is found that a mixed oxide scale is formed with a composition dependent on
O₂ concentration and pH i.e. green rust is formed with low O₂ concentration and pH >6 (as a component of the scale). Butler and Beynon (27) also showed a protective green rust film to be formed during the corrosion of mild steel in boiling concentrated MgCl₂ solutions, where a transient formation of green rust resulted in a period of marked lowering of corrosion rate. The formation of pyroaurite-type compounds and particularly green rust can thus be observed to occur under a general set of conditions. Taylor (20) states of pyroaurites that 'one cannot help being impressed by the ease with which phases of this family form; it seems necessary only to bring together appropriate di- and tri-positive ions in the presence of water at a suitable pH at or a little above room temperature, and any anions that are present are liable to be incorporated into the structure.'

1.7. Formation of Green Rusts

The formation of the pyroaurite-type compounds, green rusts (28), has received attention from a number of workers investigating the corrosion of iron-based metals in conditions of limited oxidation. However, the exact conditions of formation and stability of these compounds varies somewhat in terms of pH range and oxidation potential, suggesting that the term green rusts covers a range of compounds which may vary in structure and composition but are largely based on a formula

\[ \text{Fe(II)}_6\text{Fe(III)}_2.(\text{OH})_1\text{6CO}_3.4\text{H}_2\text{O}. \]

Mackay (29) describes these green rusts as intermediates, formed by a topotactic (accord between the initial and resulting
lattices in three dimensions (30) transformation, as Fe(OH)$_2$ attempts to precipitate in air. Evans (31) stated that green rust was formed on iron when corrosion occurs in an oxygen poor condition. Yoshioka (32) confirmed this and suggests the reaction of Fe(OH)$_2$ and the oxidised basic Fe(OH)$_3$ as being the first step in producing a green rust 2FeO.Fe$_2$O$_3$.nH$_2$O. McEnaney and Smith (24 - 26) show the green rust to be an intermediate in the formation of γ-FeOOH and Fe$_3$O$_4$ during the oxidation of cast iron in flowing waters with low O$_2$ concentration. This contrasts with Butler and Beynon (27) who show green rust to be an intermediate for α-FeOOH (Goethite) during oxidation of mild steel in salt solutions. The incorporation of the anions from solution into green rust may thus dictate the overall oxidation route. Feitknecht (33) describes two different classes of green rusts; green rust I being prevalent in chlorine containing solutions, whilst green rust II is formed in the presence of the sulphate ion. The two different structures have been characterised by a number of authors (34, 35), where the basic difference is crystallographic in that green rust I is rhombohedral whereas green rust II is hexagonal.

Attempts to characterise these green rust compounds in terms of thermodynamic parameters has also been undertaken. Charlot (36) locates the presence of a green coloured hydroxide between the region of Fe(II) ions and Fe(III) ions in neutral solution on a Pourbaix diagram (potential vs. pH). Misawa (37), whilst not considering intermediaries on constructed diagrams for Fe-H$_2$O, observed the formation of green compounds to be in agreement. Detournay et al. (38) produced a probable region of stability for
green rust II on a Pourbaix diagram, the region existing over a range of pH from 6 - 9.5. Other authors (34, 39) have studied the mechanisms of formation of iron oxides and oxyhydroxides in aqueous solutions. A summary of the different transformation mechanisms detected is presented as Figure 2 after Misawa (37). Here a distinction is made between green rusts and a green complex formed in solution. This complex has been identified elsewhere (40, 41) and is formed under neutral or slightly alkaline conditions, whereby subsequent formation of green rust is determined by the ferrous ion concentration of the solution and coexisting anions i.e. concentrated solutions and the presence of Cl\(^-\) was found to give rise to green rust I.

In summary, some general points can be emphasised concerning the formation and properties of pyroaurite-type compounds.

(1) Green rusts can be formed during the oxidation of iron where the oxygen supply is limited.

(2) These rusts can be formed in slightly acidic or slightly alkaline conditions.

(3) Pyroaurites can accommodate a variety of anions due to their layer structure and possibly, therefore, act as a 'sink' for corrosive anions either within or ingressing the coating. The ion exchange properties of such compounds is well established (42).

1.8. Objectives of this Study

The project, thus undertaken, was to initially characterise the interfacial layer formed with acidic latex coatings and attempt to
Formation of oxides and oxyhydroxides of iron in aqueous solutions. After Misawa (37).

Figure 2
determine the necessary conditions of formation. A knowledge of the nature and mechanism of formation of this film will be related to its impact on corrosion beneath the coating. It is hoped to be possible to control and improve its protective effect. Implicit within these aims are the following questions:

1) Does pyroaurite form at the polymer/metal interface and with what composition?

2) Can the coating conditions be varied to modify or enhance the formation of this interface layer?

3) Can synthetic pigments be added to the Haloflex binder to replace the need for the 'conversion' coating being formed at the interface?

The following chapters detail the analysis techniques deemed suitable for the investigation of the observed interfacial phenomena and subsequently present a series of analyses intended to answer these questions posed.
2. EXPERIMENTAL TECHNIQUES

2.1. Interfacial Analysis Techniques

A number of techniques are available to study the chemical and structural nature of the interfacial layer formed between a polymer and metal. These techniques will briefly be discussed and compared in the light of their application to the proposed formation of an interfacial layer on the application of Haloflex to mild steel.

The techniques of interfacial analysis can be divided into those which require the interface to be revealed by suitable preparation and those which can analyse a buried interface in-situ.

In the former category we can refer to Figure 3 after Watts (43). The poor spatial and chemical resolution of the combined SEM/EDXA analysis discounts its use for anything other than morphological studies of the interface region. Auger spectroscopy (AES/SAM) has been used successfully to study the polymer/metal interface by use of ball cratering techniques (44). It is thought that metallic dissolution into the polymer coating may occur to form an oxide layer and AES would be ideal to study this. However, the problems associated with analysing insulators with this technique makes its use extremely difficult. Difficulties in the provision of accurate quantitative data by AES and the lack of chemical resolution also means that such a method is not well suited to this investigation.
1. **SEM/EDXA**
   - Specimen preparation: easy
   - Resolution: poor
   - Cross section: [cross section]

2. **TEM/EELS**
   - Specimen preparation: very difficult
   - Resolution: good
   - Cross section: [microtome or ion thin]

3. **XPS/AIB**
   - Specimen preparation: varies
     - Mechanical, electrochemical or chemical separation
   - Resolution: very good

4. **AES/SAM**
   - Specimen preparation: fair
     - Ball cratering or angle lapping
   - Resolution: good

**N.B.** Electron beam analysis of organic materials is difficult without a conducting coating.

**Figure 3** Possible methods of obtaining analytical information from a buried interface. (*After (43)*).
The techniques of X-ray photoelectron spectroscopy combined with analytical transmission electron microscopy have been chosen as the route to elucidating the nature of the interfacial layer because of their respective high degree of chemical and spatial resolutions. These techniques will be described in detail later.

The techniques which can analyse a buried interface include Rutherford back scattering techniques (RBS) and extended X-ray adsorption fine structure (EXAFS). EXAFS (45) relies on the information obtained by the ejected electron from an atom, resulting from the absorption of an exciting X-ray, interfering with the standing waveform generated by the reflection from the orbitals of neighbouring atoms. This technique relies largely on 'fingerprinting' from standard compounds for identification, a factor which may restrict its use in characterising the rare and variant green rusts. RBS, which has excellent mass-depth resolution, may provide a means to study interfacial layer build up and diffusion of a metal into the polymer. However, it does not provide chemical or crystallographic resolution. This will be discussed later.

2.2. Analytical Electron Microscopy

The imaging capabilities of a transmission electron microscope are well defined in a number of texts i.e. (46), but may be summarised as resulting from the interaction of a static beam of high energy ~100kV electrons with an electron-transparent specimen. The transmitted and forward scattered electrons are recombined by the objective lens to form a diffraction pattern in
the back focal plane and a magnified image in the image plane (Figure 4). Subsequent lenses can project these images onto viewing or photographing plates.

In order to provide microanalytical information in addition to such images we must first consider the electron beam/specimen interactions which may occur (Figure 5). Whilst many of these signals are wasted on the basis of the confined space within a microscope column, any combination of these signals could be utilised. (Note Auger electrons and cathodoluminescence have been ignored). For the purpose of this study some important analytical techniques will be discussed.

2.2.1. Energy Dispersive X-ray Analysis (EDX)

As indicated in Figure 5, the generation of X-rays can occur when the high energy electron beam interacts with core shells of the specimen, resulting in a characteristic emission of X-rays for a particular element. The TEM allows X-ray analysis to be performed on thin foils or sections, where the combination of high accelerating voltage and thin specimen leads to minimal spreading of the electron beam, hence a very small X-ray source region, approximating in exceptional cases to that of the beam diameter. Under such conditions, where corrections for fluorescence and absorption of generated X-rays can essentially be ignored (47), the TEM offers a method of high resolution microanalysis with elemental specificity. Unfortunately, this method does not offer chemical state information due to the detection system electronics being unable to resolve the small chemical shifts in photon peaks.
Figure 4 The electron optical system of a TEM (After (47)).
Figure 5 Signals resulting from the interaction of a high energy electron beam with a crystalline specimen. (After (47))
The detection of the X-rays generated by the specimen is accomplished by energy dispersive spectrometry (EDS) (44), involving a Li doped Si chip with an applied negative bias with a thin contact layer of evaporated Au. The detector is generally protected from poisoning by a thin (7.5μm) Be window, which may be removed if necessary. The detection is performed by the action of X-ray photons entering the Si layer creating electron hole pairs. This charge signal is then amplified and discriminated into incident X-ray energy by multi-channel analysers on the basis of height of the charge signal pulse generated.

The use of a protective thin Be window has the effect of absorbing low energy X-rays limiting the detection of elements with atomic number Z < 10. The removal of this Be window allows detection of elements to Z = 5 and upwards albeit with very low detection efficiency, ~10% for the boron Kα signal (185eV) (49). This light element analysis involving window removal is often termed windowless EDS (or WEDS).

The EDS system can also be interfaced with a scanning transmission electron microscope (STEM) to present high resolution elemental maps to show distribution of elements about an interface. This is accomplished by setting analyser windows which record solely the X-rays generated over a defined energy range, thus indicative of a particular element.

Quantification of X-ray spectra in terms of elemental concentrations is a relatively straight forward matter and is based upon the work of Cliff and Lorimer (50) who proposed that for very thin samples:-
\[ \frac{\text{Ca}}{\text{Cb}} = K_{ab} \cdot \frac{\text{Na}}{\text{Nb}} \]

where \( \text{Na}, \text{Nb} \) are measured characteristic X-ray intensities above background;
\( \text{Ca}, \text{Cb} \) are the weight fraction of any two elements A and B in the specimen;
\( K_{ab} \) is the scaling factor, often termed the Cliff-Lorimer factor, and is dependent on the two elements, the operating conditions and detector response. This factor is usually determined experimentally whereby K is measured, for convenience, in combination with a single element i.e. Si, using alloys or minerals of known composition. Once evaluated, the \( K_{ab} \) term may be replaced by \( K_{as1/Kbs1} \).

Energy dispersive X-ray analysis, therefore, presents a means by which suitably prepared sections can be analysed to give chemical composition on a microanalytical base and elemental distribution 'mapped' at a spatial resolution determined by image storage capabilities i.e. Pixel images.

2.2.2. \textit{Microdiffraction}

Diffraction studies within the context of the electron microscope (for greater detail see (51)) have a number of intrinsic differences when compared to the techniques of X-ray and neutron diffraction. The fundamental steps in electron diffraction are simply:-

(i) a beam of electrons can be focused on to a small, identifiable region of the sample within the electron microscope.
under conditions of diffraction, Bragg's law is obeyed

\[ n\lambda = 2d \sin \phi \]

which for small angle diffraction, \( \phi \) is generally less than 1 degree, can be simplified to

\[ n\lambda = 2d \phi \]

The diffraction can then be treated in a number of possible experimental arrangements to give structural information. The most common are (Figure 6):-

(i) Selected area diffraction (SAD).

A parallel beam illuminates a thin specimen forming a focused diffraction pattern in the back focal plane of the objective lens (Figure 6a). A single crystal thus forms a spot pattern whilst a polycrystalline sample gives rise to a ring pattern.

(ii) Convergent beam electron diffraction (CBED).

A highly convergent beam is focused on to a very small region of the sample forming a pattern on the back focal plane consisting of discs. Each separate point within a disc contains information about diffraction from the same point on the sample but with a different angle of incidence (Figure 6b). The spatial resolution of CBED can reach a limiting value of \( \sim 10\AA \) compared with a limiting resolution of \( \sim 0.5\mu m \) in selected area diffraction.

Specimen requirements for electron diffraction are dictated by the inelastic scattering processes arising from electron beam/specimen interactions, which tend to limit specimen thickness to below 1\( \mu m \).

The interpretation or indexing of a diffraction pattern can be
Figure 6  Electron optical paths for convergent beam and selected area diffraction.
complex and is dealt with in (51). However, in all diffraction patterns we can use the equation

\[ r \, d = \lambda \, l \]

which shows the relationship between \( d \), the spacing of the scatterers in the sample, and \( r \), the spacing of the equivalent features in the diffraction pattern. \( l \) is the camera length and \( \lambda \) is the electron wavelength.

Microdiffraction is thus a means of determining structural information obtained from a very small area of the analysed specimen.

Analytical electron microscopy can, therefore, gain insight into the polymer/metal interface by:-

(i) high resolution imaging to assess the state of the interface.
(ii) EDX analysis to give microanalysis at selected points around the interface region.
(iii) EDX mapping to give the distribution of elements in the interface region.
(iv) Electron diffraction to propose the structure of the interface.

2.3. **X-ray Photoelectron Spectroscopy (XPS)**

X-ray photoelectron spectroscopy concerns itself with a special form of photoemission whereby X-ray photons incident on an atom causes the ejection of an electron from a core level. The kinetic energy, \( E_k \), of the emitted electron is a function of the
initial photon energy, $h\nu$, and binding energy of the core level, $E_b$, overcome to enable the escape into free space of the electron being given by the Einstein relationship:

$$E_b = h\nu - E_k - W$$

where $W = \text{spectrometer work function}$.

As all three parameters on the right hand side of the equation can be measured or are known, it is a simple calculation to determine binding energies of emitted photoelectrons. XPS spectra are thus usually presented as a graph of intensity (counts) versus electron binding energy (eV) (Figure 27). The means by which electron energy distributions are measured and recorded puts severe constraints on the instrumentation required for this purpose and thus deserves mention not only in its own right but also to gain further insight into the applicability of this technique.

2.3.1. The X-ray Photoelectron Spectrometer

The spectrometer used for XPS is designed to facilitate the collection of photoelectrons arising from the interaction with an incident photon (X-ray) source, and thus primarily comprises of an analyser chamber (Figure 8) with attached X-ray gun and electron analyser. The photoelectron process imposes stringent vacuum requirements on such an analyser chamber for two basic reasons. Firstly, electrons are easily scattered by gas molecules and therefore must meet as few as possible on their way to the analyser i.e. the mean free path of the electron in the vacuum must be considerably greater than the dimensions of the
Figure 8 The ESCALAB Mk.II spectrometer.
spectrometer. More importantly for vacuum requirements is the fact that XPS is very much a surface sensitive technique and therefore sensitive to surface contamination. Gas kinetic theory predicts that a monolayer of gas will accumulate on a surface in 1.5 seconds at a pressure of $10^{-6}$ torr at room temperature. The majority of XPS analyses are performed, on this basis, at a vacuum of $\sim10^{-10}$ torr and are classed within the regime of ultra-high vacuum (UHV).

Details of UHV pumping systems (52) and consideration of the spectrometer construction can be found elsewhere (53).

2.3.1.1. X-ray sources

From the stated Einstein relationship in section 2.3, it can be deduced that the width i.e. resolution of the $E_k$ line of an ejected photoelectron will depend on the width of the $h\nu$ line of the photon source. The general desire for energy resolution to be better than $\sim1.5\text{eV}$ for XPS, largely dictates the choice of anode material to have a line width $<1.0\text{eV}$ in order not to introduce broadening. The choice of X-ray source is restricted on such grounds to yttrium Må, zirconium Må, magnesium Kα, aluminium Kα, and silicon Kα. However, Y and Zr lines, although narrow, are too low in energy to be useful. Furthermore, Si anodes are very difficult to fabricate thus leaving Mg and Al as universal anodes.

Magnesium Kα (line energy 1253.6eV) and aluminium Kα (1486.6eV) sources are usually combined as twin anodes i.e. both Mg and Al elements to enable switching between the two. An aluminium window $\sim2\mu$m in thickness, is placed between the anode
and specimen to eliminate stray electrons, contamination and heating effects detrimental to the sample. Other sources of X-rays for specialist applications can be found in (54).

2.3.1.2. The Electron Energy Analyser

Two types of electron energy analysers are currently in use for XPS; the cylindrical mirror analyser (CMA) and the hemispherical sector analyser (HSA), the latter offering relatively high sensitivity with high resolution and therefore often preferred in XPS. Both analysers modes are detailed in (50).

Figure 9 shows a schematic diagram of an electron spectrometer showing relative positions of photon source, sample and HSA detector. The mode of operation of the HSA must be considered in the context of resolution requirements in XPS analysis.

Absolute resolution $\Delta E$ is usually the full width half maximum -FWHM- of an XPS peak. The relative resolution is then defined as

$$ R = \frac{\Delta E}{E_0} $$

where $E_0$ = kinetic energy of peak

XPS requires identification of chemical states of elements by peak shifts and curve separations at any energy in the spectral range (see section 2.3.3.) and, therefore, requires the same absolute resolution across the spectrum. To match the absolute resolution to the line widths of the X-ray sources at the maximum kinetic energies would require a relative resolution of $\sim 6 \times 10^{-4}$, which is difficult to achieve without making the analyser very
Figure 9 Schematic diagram of the spectrometer (Figure 8) showing the major components. (After (69)).
large. The HSA is, therefore, combined with a pre-retardation stage - a retarding field analyser - to achieve adequate resolution i.e. a 50 eV pass energy and absolute resolution of 0.7 eV requires a relative resolution of only $\sim 1.5 \times 10^{-2}$. This retardation in XPS operates under what is termed constant analyser energy or CAE mode, whereby a constant voltage is applied across the hemispheres of the analyser allowing only electrons of a particular energy to pass through it. Thus, referring to Figure 9, the photoelectrons are emitted from the sample and transferred to the focal point of the analyser by the lens assembly. At this point they are retarded before entering the analyser itself. Those electrons with an energy matching the pass energy are transmitted through the analyser and counted by the multichannel detector. Acquisition of a spectrum is then achieved by ramping the potential of the retarding field analyser.

This form of spectroscopy also possesses a number of special features which offer more than just simple chemical identification.

(i) Depth of analysis: although X-rays can penetrate deeply into a specimen, the inelastic mean free path of a photoelectron is very small, typically being in the range of 0.3-3.0 nm. Thus the analysis depth in XPS is very much surface specific. The intensity of electrons, $I$, emitted from a depth, $d$, is given by the Beer-Lambert equation:

$$ I = I_0 \exp\left(-\frac{d}{\lambda \sin\phi}\right) $$

where $I_0$ is the intensity from an infinitely thick, clean substrate; $\lambda$ is the inelastic mean free path and $\phi$ is the angle.
subtended by sample surface and analyser optics (take-off angle). Analysis of this expression yields a method of limited depth profiling by varying the parameters of incident photon energy and take-off angle. Considering the effect of photon energy, it is first necessary to integrate the Beer-Lambert Equation over a number of multiples. From this it is predicted that 95% of an XPS signal from a surface emanates from a depth of 3\( \lambda \), 85% from 2\( \lambda \) and 65% from \( \lambda \). Since mean free path \( \lambda \) is a function of electron wavelength and varies with \( E^{1/2} \), it is evident that higher energy photoelectrons (i.e. higher \( E_{\text{Kx}} \)) can escape from greater depths. A compositional depth profile can therefore be easily achieved by switching X-ray sources to a more energetic photon energy (see 2.3.1.1.) (e.g. on the C1s line of a typical polymer, the ‘analysis depth’ can be increased from 4 to 5 nm by switching from MgK\( \alpha \) to AlK\( \alpha \)).

Analysis of the Beer-Lambert expression in terms of take-off angle is simply visualised in that as the take-off angle is reduced from \( \phi = 90^\circ \) to \( \phi = 0^\circ \) the effective escape depth of the photoelectrons is increased thereby further enhancing the surface specific nature of the photoelectron emission. A typical analysis carried out at a value of \( \phi = 45^\circ \) indicates that 75% of the total XPS signal comes from a thickness of \( \lambda \).

2.3.2. Chemical Shift Information

The basis of the chemical shift information that can be obtained from XPS spectra is that non-equivalent atoms of the element in a solid give rise to core-level peaks with measurably
different binding energies. This non-equivalence of atoms can arise in several ways i.e. difference in formal oxidation state, molecular environment, lattice site and so on. To detect and measure shifts requires accurate reference to a standard peak position and ultimately back to the fermi level of a conductor. Standards commonly used are the gold Au 4f line at 84eV and the Cu2p and Auger lines at 932.67eV and 914.4eV on a binding energy scale respectively.

However, problems with charging occur in non-conducting samples as electron loss at the surface is not countered by charge flow from earth. This is observed as a peak shift to higher binding energies as the photoelectron escaping from the surface passes through a positive charge cloud. This charge problem can be countered in two ways:

1) charge compensation to minimise the influence of charging, or
2) use of internal standards not sensitive to charging.

The use of flood guns to neutralise surface charging is complex (55) and appears not to be sufficient for the acquisition of accurate chemical state information with conventional twin anode X-ray sources.

Internal standards may be used to charge reference a sample. The most useful is to reference carbon, usually present as adventitious contamination, back to its value of 285eV. A problem encountered here may be that insulating surfaces can show differential charging if there is inhomogeniety across the analysed region, also the form of carbon may lead to an uncertainty of as much as 0.4eV in the value quoted above.
Another internal standard that may be used is the charge independent Auger parameter (56), which is itself a method of obtaining chemical state information. The parameter does not use a single chemical shift, but rather a relative shift of Auger and photoelectron spectra. The derivation of the parameter is shown in (56) giving a definition of the Auger parameter $\alpha$ as,

$$\alpha = E(KLL) - E(1s)$$

being the difference between the K.E. of the most intense Auger peak (KLL) and the K.E. of the most intense photoelectron peak (1s). Modified versions of this parameter also exist but are largely based on the same theme. Auger parameters are, therefore, determined and tabulated as reference tables. A modified Auger parameter ($\alpha^*$) has been defined to overcome the problem of negative values of $\alpha$, and the variation of $\alpha$ with photon energy;

$$\alpha^* = KE_{(KLL)} + BE_{(1s)}$$

The chemical shift experienced by peaks is illustrated in Figure 10 and shows how computer curve fitting can be performed to determine the relative contribution of the constituent orbital peaks to a mixed valence elemental peak. A knowledge of the distance between peak centres (the peak shift) is necessary to perform such iterative procedures and these have been determined for a great number of oxidation states of elements, and are available in several tabulations (57, 58).

One particular form of peak shift phenomena is termed the shake-up satellite and is a consequence of the reaction of the associated valence electrons to the apparent increase in nuclear charge when an atom undergoes the loss of a core electron by
Figure 10

Peak fitting for O1s peak showing lower energy oxide and hydroxide constituents.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Centre (eV)</th>
<th>FWHM (eV)</th>
<th>Hght %</th>
<th>G/L %</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>535.3</td>
<td>2.20</td>
<td>61</td>
<td>20</td>
<td>44</td>
</tr>
<tr>
<td>2</td>
<td>537.3</td>
<td>2.20</td>
<td>79</td>
<td>20</td>
<td>56</td>
</tr>
</tbody>
</table>

100% Height (Counts) : 232
100% Area (keV/sec) : 0.0740
Reduced Chi Squared : 0.99

HALO ON MILD STEEL
MILLED -2.5C
INTERFACE REGION SA
photoemission. The reorganisation of the valence band may result in excitation of a valence electron into a higher unfilled level (shake-up). The energy associated with the shake-up is therefore not available to the emitted photoelectron and thus a shake-up satellite appears at a higher binding energy (lower K.E.). Very strong satellites are observed for certain transition metal and rare earth compounds which have unpaired electrons in the 3d or 4f shells respectively. Their appearance may be used as a diagnostic tool, distinguishing valence states of some elements. This is particularly true for iron where the satellite position in the Fe2p peak can distinguish the di- and trivalent valence states. This is illustrated in Figure 11, after Castle et al.(70).

XPS has, therefore, been shown to be a surface sensitive technique with the ability to distinguish chemical state information. The combination of XPS with an atomic sputtering device would therefore lend itself to high resolution depth profiling, which although destructive, could penetrate to considerable depths. Such a sputtering system is argon ion etching (59).

2.3.3. Argon Ion Sputtering

Atomic layer removal (sputtering) is achieved in the XPS spectrometer by means of an attached argon ion gun (Figure 8), whereby inert Ar gas ions are generated by a collisional excitation with electrons of typically 100eV energy from a hot or cold filament. The positive ions are then accelerated to between
Figure 11  Iron Fe 2p3 peaks showing relative position of satellite in di- and trivalent iron.
0.5 and 5KeV and focused on the sample creating a sputtering diameter of ~1-5mm. Depth profiling is thus achieved by analysing the residual surface left after a certain sputtering time.

2.4. A.C. Electrochemical Impedance Spectroscopy

2.4.1. The Polymer Coated Metal as an Electrochemical Cell

Polymers can generally be classed within the group of materials known as dielectrics, which, in the ideal case, are perfectly homogeneous materials possessing an infinitely high resistance to charge transfer in low D.C. electric fields. Conversely, under alternating current conditions, all the energy is transmitted through the film without power losses. Real dielectrics, however, do have finite resistance and possess heterogeneities and defects, such that A.C. power losses are incurred due to resistance heating and polarisation processes (60). This energy dissipation is termed the dielectric loss. The contributory elements of dielectric loss may be generalised and thus defined as being due to the polarisation (i.e. movement) of charge carriers in the electric field (61). The inherent charge carriers and subsequent uptake of charged species into a polymer film could therefore be monitored by measurement of dielectric losses in the film.

It has also been postulated (62) that a paint coating does not behave as a uniform dielectric, but exhibits electrical conductivity as a consequence of polymer breakdown or electrolyte infiltration into pores. The paint film can then be visualised as
a number of conducting pathways within a dielectric matrix. On complete penetration of an electrolytic conducting path to the substrate, an electrochemical cell is evoked and corrosion is the likely occurrence. As corrosion proceeds electrode polarisation (see section 1.2.) may occur. In particular, an interfacial oxide may form, thus again presenting a capacitive dielectric barrier to charge transfer.

The charge transfer and electrode (anode, cathode) reactions can indicate mechanisms and rates of corrosion requiring measurement of these parameters for a greater understanding of the anti-corrosive nature of a polymer film. These fundamental charge transfer reactions at an electrochemical interface may be described in terms of (63):-

i) transport of species in the bulk of the electrolyte to the electrode interface.

ii) adsorption of reactive species on the electrode.

iii) electrochemical and chemical reactions.

The technique of A.C. electrochemical impedance spectroscopy is able to study each of these elementary phenomena in isolation from the others in that each of these processes (and others) will have different relaxation times characteristic of the movement of the associated electrons or ions. The application of these sequential reactions is, in the case of a coated metal, hindered by the polymeric diffusion barrier present and hence the resistance inhibition that it offers can be determined.

Essential to this outcome is the ability to model particular metal/coating systems by an equivalent electrical circuit.
2.4.2. Representation of a Coated Substrate by an Equivalent Electrical Circuit

An electrode interface during an electrochemical reaction is analogous to an electronic circuit consisting of an array of resistors and capacitors combined in a manner dependent on the state of corrosion proceeding. This representation, therefore, allows established A.C. circuit theory to characterise an electrochemical system in terms of its equivalent circuit. In particular, circuit theory can predict the response of a given circuit to an applied alternating current or voltage as a function of frequency. The rigorous mathematical treatment of this can be found in texts of A.C. theory or control engineering e.g. (64). The linear response of a system to a sinusoidal input

\[ x(t) = A \sin \omega t \]

yields a response

\[ y(t) = B \sin \omega (t + \phi) \]

where amplitude B is different from input, A, and the sinusoidal wave is displaced by some angle \( \phi \). From this, a transfer function can be defined

\[ H(\omega) = \frac{B}{A} e^{j\phi} \]

where \( |H(\omega)| = \frac{B}{A} \)

If we define the impedance of a system for an alternating current as

\[ E = IZ \]

where E and I are waveforms for potential and current respectively, and Z is the impedance (the A.C. equivalent of resistance) we can use the linear frequency response to show that
if \( x(t) \) is a current and \( y(t) \) a voltage then \( H(\omega) \) is an impedance value. It also follows that for a small voltage perturbation

\[
Z(F) = \frac{\Delta E}{\Delta I} = |Z|e^{j\phi} = \frac{\Delta V|e^{j\omega t}}{|\Delta I|e^{j(\omega t-\phi)}}
\]

where \( j = \sqrt{-1} \)

\[
\omega = 2\pi F
\]

or in terms of real, \( R \), and imaginary, \( I \), parts impedance can be defined as

\[
Z(F) = R(F) + jI(F)
\]

Mathematical treatment may also be applied to express the impedance of circuit elements to an A.C. waveform (65) i.e.

Resistor \( Z_R = R \)

Capacitor \( Z_C = \frac{1}{j\omega C} \)

Inductor \( Z_L = j\omega L \)

Their impedance of any combination of circuit elements can thus be defined by a linear combination of elemental expressions to yield a complex phase response.

Table 1 shows a number of circuits which have been analysed to yield impedance relationships. The relationship of paint films to such equivalent circuits must therefore be discussed with the following examples.

Figure 12 shows a simple electrochemical cell where \( R \) is the uncompensated resistance between the working electrode and
<table>
<thead>
<tr>
<th>CIRCUIT</th>
<th>IMPEDANCE EQUATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>( Z = Z' + Z'' = R + 0 \ j )</td>
</tr>
<tr>
<td>C</td>
<td>( Z = Z' + Z'' = 0 - \frac{j}{\omega C} )</td>
</tr>
<tr>
<td>C</td>
<td>( Z = Z' + Z'' = R - \frac{j}{\omega C} )</td>
</tr>
<tr>
<td>C</td>
<td>( Z = Z' + Z'' = R + \frac{R}{1 + \omega^2 C R^2} - j \frac{\omega CR^2}{1 + \omega^2 C R^2} )</td>
</tr>
<tr>
<td>R</td>
<td>( Z = Z' + Z'' = R_1 + \frac{R_2}{1 + \omega^2 C R_2^2} - j \frac{\omega C R_2^2}{1 + \omega^2 C R_2^2} )</td>
</tr>
</tbody>
</table>

**Table 1** Impedance relationships for a number of simple circuits.
Equivalent circuit for a simple electrochemical cell

Figure 12
reference electrode and $R_p$ is the polarisation resistance or charge transfer resistance at the electrode/solution interface. $R_p$ has been used to calculate electrochemical reaction rates (66). $C_d$ is the double layer capacitance at this interface and can provide information on film formation processes and integrity of organic coatings (89, 16).

Figure 13 shows the situation where penetration of the electrolyte into pores has occurred (66). The parameters $C_c$ and $R_p$ are coating capacitance and pore resistance respectively.

It is therefore apparent that the physical situation occurring on a polymer coated substrate can, in most cases, be referred to an equivalent circuit model. The individual elements and thus the model can also be expressed in terms of their impedance, $Z$. This is utilised in A.C. impedance spectroscopy.

2.4.3. Experimental Arrangement.

The impedance of an electrochemical system at an imposed frequency was shown in section 2.4.2 to be defined by the magnitude of the impedance vector, $|Z|$, and the phase angle, $\phi$, or by the real (resistive), $R_e(f)$ and imaginative (reactive), $I_m(f)$ components of impedance. Instrumentation capable of measuring such parameters are termed Lock-in Analysers. In electronic terms this is a narrow band filter (67), which relates a reference signal to a measured signal of interest. Essentially, the analyser 'chops' or modulates the measured signal at a frequency determined by the reference signal and compares the two waveforms. The output of the analyser is then in the form of D.C. voltage signals relating
Equivalent Circuit for a Polymer Coated Metal
phase difference and ratio of peak amplitudes between the two sinusoidal waves. These two parameters are all that is required to describe the impedance of the electrochemical system and, therefore, the appropriate diagram can be constructed. A frequency response analyser, incorporating a lock-in analyser, scans a range of frequencies and detects the response at certain frequency intervals to give the frequency dependence of impedance.

The experimental set-up enabling impedance measurement of an electrochemical cell can be illustrated with the schematic diagram, Figure 14. Two possible arrangements are shown here based on differing main features:

(a) The first arrangement utilises the high impedance of an operational amplifier circuit. The action of the amplifier is to provide negative feedback to ground and by using its output as source or sink acts to keep the measured voltage on the two output terminals (marked + and - ) equal. Current flow between these terminals is therefore zero (or negligible). From Kirchoffs laws it can easily be deduced that at point V

\[ I_1 = I_o \]

and therefore,

\[ \frac{V_y}{|Z|} = \frac{V_x}{R_s} \]

simply rearranging gives

\[ |Z| = \frac{V_y}{V_x} \cdot R_s \]

hence knowing the values of feedback resistor \( R_s \), \( V_x \) and \( V_y \) can be measured by a lock in analyser (together with values of phase
Figure 14 Block diagrams of two possible A.C. impedance measuring circuits.
angle, $\phi$,) for scanned frequencies.

(b) The use of the potentiostat in the second diagram is a variation on this operational amplifier theme. The reference electrode within the cell arrangement holds a constant potential between the working and counter electrode, by variation of current uptake (or change in resistance) as the impedance of the cell varies. $V_x$ and $V_y$ are again measured by a lock-in analyser.

The operational amplifier circuitry may have advantages over the potentiostat arrangement if coatings with excessively high impedance values are measured. This is due to the fact that if the resistance of the coating is too high, the adjustment of the potentiostat may be impossible. Furthermore, the frequency response of commercially available potentiostats is claimed to be poor (68) leading to phase shifts at high frequencies.

### 2.4.4 A.C. Impedance Plots

A frequency response analyser collects raw data at each measured frequency consisting of:-

(a) The real and imaginary components of voltage $E'$ and $E''$.
(b) The real and imaginary components of current $I'$ and $I''$.

From this data it is possible to compute the phase shift response, $\phi$, and total impedance, $Z$, for each applied frequency.

Different ways of plotting impedance can then be performed. Examples of the major plot methods will be presented and discussed.
2.4.4.1 The Nyquist Plot

The Nyquist plot is a complex (Argand) impedance plane diagram, plotting the imaginary part of impedance $Z''$ versus the real part $Z'$. Figure 15 shows the expected response of the simple circuit shown as Figure 12. The semi-circular shape can be ascribed to the fact that at higher frequencies the polarisation processes, associated with charge movement, cannot keep up with the excitation waveform and are thus redundant - leaving $R_p$ transparent to the technique. At lower frequencies polarisation processes are able to keep pace with the waveform and therefore $R_p$ contributes to the measured impedance as a perfect resistor. In between these two extremes capacitive losses are indicated.

Analysis of the resulting plot yields values for $R_o$, $R_p$ and $C_{dl}$.

2.4.4.2. The Bode Plot.

Figure 16 is a Bode plot for the same data as Figure 15. This format enables the examination of both the absolute impedance $|Z|$, and phase shift, $\phi$, of resultant waveforms as a function of frequency.

The log $|Z|$ versus log $\omega$ curve can yield values of $R_p$ and $R_o$. At intermediate frequencies, the break point of this curve should be a straight line with a slope of $-1$ (71). Extrapolation of this line to the log $|Z|$ axis at $\omega = 1$ (log $\omega = 0$) yields the value of $C_{dl}$ from the relationship

$$|Z| = \frac{1}{C_{dl}}$$
Figure 15 Nyquist A.C. impedance profile for a simple electrochemical cell (Figure 12).
Figure 16  Bode plot response for a simple electrochemical cell (Figure 12).
It can therefore be seen that modelled systems can easily be interpreted by simple plot techniques. Non-ideal systems are very much harder to break down into component areas. The response and interpretation of Haloflex coatings to A.C. spectroscopy will be dealt with in a later section.
3. CHARACTERISATION OF THE INTERFACIAL LAYER FORMED IN-SITU BETWEEN HALOFLEX/STEEL

The investigative regime proposed for this interfacial study is based upon the analysis of interface composition and structure by analytical TEM and XPS followed by coating performance assessment by A.C. electrochemical techniques. This study will, therefore, be presented in terms of the objectives outlined in Chapter 1.

3.1. TEM Analysis

The initial characterisation of the interfacial film formed in the Haloflex/steel system was undertaken using a cross-sectional analysis of the oxidation of iron in the presence of the Haloflex binder. Use of the binder rather than the whole paint has the benefit of eliminating the effects of pigmentation. By analysing various oxidative conditions it is hoped to establish the spatial position and route of formation of the interfacial species.

3.1.1. Specimen Preparation

The necessity for microtomy in the preparation of polymer/metal samples imposes severe limitations on the thickness of metal that can be present in the cross section. The required thin section was achieved by evaporation of iron onto a polystyrene substrate which was present as a coating on a glass slide (Figure 17). These coated slides are then dipped into the
configuration of dipped slide

Figure 17

colour transform of dry slide

Figure 18
Haloflex binder and dried at an inclined angle to produce a wedge-shape distribution of coating, caused by the flow of binder to the base of the slide. The thickness of iron evaporated was varied to find an 'optimum' layer thickness, which would react with Haloflex to a sufficient degree as to leave some residual iron, yet was still thin enough to be microtomed. This optimum iron thickness was found to be in the region of ~150nm. The range of attack by the binder on the iron can be clearly detected by the visual appearance of the dry film as indicated in Figure 18. After an initial green colouration in the wet state, a clear colour differentiation along the slide length was observed with residual iron remaining at the top, followed by a progression of colours, black - brown/orange - transparent at the base (Figure 18), indicating progressive consumption of iron towards the bottom of the slide.

This technique, therefore, allows specimens to be removed and microtomed to compare the different degrees of oxidation in the interfacial film. The thicker the film, the longer the binder is in contact with the substrate in a liquid state, and consequently the easier it is for the reaction that leads to the formation of an interfacial layer (and consumption of iron) to proceed, and perhaps subsequent diffusion to occur.

It must also be noted that the Haloflex binder, originally at a pH of ~1.5, was buffered to a pH of ~5.5 as is the case with Haloflex paints. Buffering was enabled by addition of alkaline potassium hydrogen phthalate (72).
3.1.2. Analysis and Results

Analysis of the cross sections was performed on JEOL 200CX and Philips EM400T microscopes under conditions of low beam current in order to avoid beam damage to the polymer. The specimens examined show three distinct regions namely; residual iron, the latex cells and an interfacial layer, (although in initial analyses poor choice of microtome resin was evident in polymer swelling of the latex, causing most areas of these three phases to become detached from each other). Figures 19 and 20 show typical micrographs of the interfacial areas once an acceptable resin had been adopted.

X-ray mapping using STEM facilities on the Philips 400T was performed on various interfacial areas. Pixel images of 512 x 512 resolution were recorded and processed as video images (Figure 21). These clearly demonstrate the interfacial enrichment of iron and chlorine.

Quantitative X-ray analysis was performed on microtomed samples on the 400T using a windowless detector, thereby allowing the analysis of oxygen to be undertaken. Different regions identified visually and by electron diffraction were analysed, with each region being analysed over a number of collection points and undergoing ten minute collection times at each point to establish a statistical accuracy in the compositional determination. The analysis was also performed on samples microtomed from different areas of our original dipped slide (Figure 18).
Figure 19 TEM micrograph of initial stages of interface oxide formation.

Figure 20 TEM micrograph of substantial interfacial oxide formation.
Figure 21  STEM maps of interfacial areas showing enrichment in Fe and Cl.
The resulting EDX analysis showed the presence of definite discernible regions within one interfacial zone on many samples, the differentiation being determined by Fe:O ratios.

Four different regions were identified in this manner:

<table>
<thead>
<tr>
<th>Region</th>
<th>Ratio Fe:O</th>
<th>Interaction Level</th>
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<tr>
<td>I</td>
<td>10 : 1</td>
<td>Least attack</td>
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<tr>
<td>II</td>
<td>1 : 2.0</td>
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<tr>
<td>III</td>
<td>1 : 1.3</td>
<td>Intermediate attack</td>
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<tr>
<td>IV</td>
<td>1 : 4.9</td>
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Regions I and II were identified as being present on samples which had received the least attack by the binder (i.e. the thinnest Haloflex coating). Regions III and IV were identified as being present on samples designated intermediate attack by binder. All four regions are clearly observed in the TEM micrographs of Figure 22. There is no identifiable interfacial zone on samples from areas of maximum attack, merely a well defined cellular latex structure.

In areas II, III and IV, chlorine content was found to be in the region 2-4%. This chlorine content was tested for 'inorganic nature' by prolonged exposure to the electron beam. Organic material was readily identified in this manner by a time dependent lowering of Cl concentration.

Errors in this analysis may arise from a great number of sources. A great problem in light element analysis is the determination of the experimental elemental sensitivity factor, or
Figure 22  Different regions of interface observed by EDX.
K-factors as they are termed. A standard K-factor has been used for oxygen, which neglects absorption effects from the neighbouring Fe atoms. Also, the presence of a large volume of polymeric material in the samples (thought to be mixed in with the growing oxide) causes a higher oxygen content to be observed by high energy backscattered electrons being able to fluoresce this oxygen containing polymer. These points will be treated in the later discussion stage.

Structural determination by electron diffraction was performed using a focused electron beam ~20nm in diameter. Under such conditions the resulting diffraction pattern consists of a series of discs rather than points; a representative electron diffraction pattern is presented in Figure 23. The separation of centres, r, is given by:

\[
r = \frac{\lambda l}{d}
\]

\(\lambda\) = wavelength of electron beam
\(l\) = camera length
\(d\) = interplanar spacing

A summary of the large number of diffraction patterns recorded, and their coincidence with the reflections expected from a series of iron compounds is presented in Table 2. In this tabulation the reflections consistently seen in the convergent beam diffraction patterns of the interfacial region are listed in column 1. Possible iron compounds are identified in row 1 and reflections present in both the experimental patterns and those expected from the compounds (73) are identified by a cross. However, it must be remembered that for certain compounds many reflections will be expected that are absent from the experimental
Figure 23 Convergent beam electron diffraction (CBED) pattern.

camera length = 975mm

Figure 24 Convergent beam diffraction pattern identifying pyroaurite.
### Possible Iron Compounds

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<th>Observed Reflection (angstroms)</th>
<th>GR1*</th>
<th>Fe(OH)₂</th>
<th>αFe₂O₃</th>
<th>cFe₂O₃</th>
<th>βFe₂O₃</th>
<th>Fe₃O₄</th>
<th>FeO*</th>
<th>FeCl₃</th>
<th>FeCl₂</th>
<th>αFe₂(OH)₃Cl</th>
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*GR1 = Fe₃.6Fe₀.₅(O,OH,Cl)₉

**FeO = Wüstite**

Note: Reflections consistently seen in CBD patterns are listed in column 1. Possible iron compounds are listed in row 1 and reflections present in both the experimental patterns and those expected from compounds are identified by a cross.
data (e.g. γFeOOH has some 23 reflections, only 5 of which are present in these results). On the other hand, some compounds (e.g. green rust I) may have only a few reflections, practically all of which are seen in Table 2. Other compounds are distinct possibilities (e.g. αFeOOH) as the majority of reflections are satisfied. The appearance of a reflection corresponding to an interplanar d spacing of 7.10 Å (Figure 24) identifies unambiguously the presence of green rust as a component of the interfacial region and therefore a large number of observed reflections can be accounted for. The calculation of d spacing for pyroaurite is shown schematically as Appendix 2.

It must be noted that electron diffraction determinations contain a number of inherent inaccuracies, particularly associated with the visual estimate of disc spacing using a graduated eye piece. Thus, the number of coincidental reflections is high, requiring some other means to sensibly propose the combination of products in the interface zone. Thus, a supplementary study of interfacial chemistry was undertaken using XPS.

3.2. X-ray Photoelectron Spectroscopy

3.2.1. Specimen Preparation

Haloflex, buffered to a pH of ~5.5 by the addition of potassium hydrogen phthalate and sodium hydroxide, was applied to mild steel shim stock by means of wound wire bar coaters; being given two coats of 40µm nominal wet thickness and allowed to dry in air. Samples were then subjected to an iodine/methanol
dissolution treatment (see Figure 25), whereby a sample under inert (N₂) atmosphere is immersed in a heated (~ 35°C), saturated solution of iodine in double distilled methanol (74). This aggressive media allows attack on the metal substrate to occur without formation of a protective oxide and thus proceeds without inhibition whilst the interfacial oxide and polymer coating remain essentially unaffected. Subsequent washing of the remaining sample in methanol produces a film of interfacial oxide on the polymer coating which can be analysed by XPS.

3.2.2. Results and Analysis

Oxide/Haloflex films were analysed in a V.G. Scientific ESCALAB Mk. II spectrometer using an AG21 cold cathode argon ion beam to produce a compositional depth profile through the polymer towards the oxide interface. XPS analysis involved a survey scan for identification of elements and general artefacts over a range of 0.1eV - 1000eV (BE) supplemented by more detailed high resolution narrow scans around elemental peaks of interest (see Appendix 3 for acquisition parameters). Subsequent etching by a 3kV argon ion beam focused at 1.5kV and at a pressure of 10⁻⁶ torr enabled a depth profile to be undertaken. The exact etch rate achieved under these conditions is unknown since no sputter current could be detected from the polymer sample. However, an etch rate of 3.5nm/min is quoted by Fakes et al. (75) for etching polymeric materials, so this may be used as a rough guide. The depth profile obtained is shown as Figure 26, with the depth axis being related to etch time. It can be seen from this profile that
Figure 25  Iodine methanol stripping rig.
the expected change in iron and carbon is observed - an increase in Fe on approaching the interface and decrease in carbon as polymer is lost. However, it can also be seen that chlorine (and oxygen) increase as the polymer (i.e. carbon) content is reduced, thereby suggesting it is associated with the inorganic layer.

Figure 27 shows the wide scan of Haloflex on steel and Figures 28-30 then show the higher resolution scans of the Fe2p peaks for some selected stages of etching. The series shows the growth, initially of a lower energy shoulder on the main peak, which eventually becomes dominant. This lower energy peak then remains dominant in a situation where at least two chemical states of iron exist, as evidenced by the two components of each orbital peak. Eventually the higher energy component begins to grow again at the end of the etch series (after 178 minutes etching). With reference to Figures 28-30, the behaviour displayed suggests a reduction in oxidation state of the iron as the depth profile continues. By charge referencing the peaks in question to the carbon 1s peak at ~285eV, it appears that the initial, mainly divalent, Fe (spectra X00701) is transformed to a mixed metallic Fe (ϕ) and divalent Fe(II) state after 8.5 minutes etch (spectra X00855). On prolonged etching, some divalent Fe(II) character is stored resulting in the broad peaks of spectra ANM 020. (This may be in some part due to a suspected air leak in the argon feed to the etching gun). However, the possibility of the beam reduction occurring in etching will be discussed in section 3.4. Corresponding scans for oxygen (O1s), chlorine (Cl2p) and carbon (C1s) are shown as Figure 31. The peak broadening or splitting can be observed in these scans, indicating a chemical binding
Figure 27
Wide scan for HaloFlex on Fe

HALOFLEX ON FE
AR ETCH = 86 MINS
3KV 10-6 TORR
Figure 28  Etch series on Fe2p peaks
Figure 30
Figure 31  O1s, C1s and C12p peaks for Haloflex on Fe
change. The exact nature of this change will be discussed later.

3.3. Rutherford back scattering (RBS)

Rutherford back scattering was performed using a 2MeV van der Graaf accelerator unit on coated specimens prepared by similar means to XPS specimens prior to etching (section 3.2.1.). The resulting RBS spectrum for Haloflex on steel is presented as Figure 32 and shows a peak corresponding to Cl atoms at the interface (as predicted by the RUMP computer simulation (76)).
Figure 32: RBS profile relating mass and depth, indicating enrichment by Cl and Fe.
3.4. Discussion of Characterisation

The results of the various analyses can be used to complement each other in proposing a model of interfacial build up even though the results of single analysis are, on their own, insufficient to elucidate the interface composition.

The electron diffraction information obtained can be viewed in the light of the mechanisms of formation of oxides and oxyhydroxides of iron proposed by Bernal et al. (34) and later developed upon by Misawa et al. (35), although it must always be borne in mind that the oxidation occurring in this system transforms from wet to dry oxidation as the Haloflex dries and indeed, on exposure of the interface after microtomy. Applying our knowledge that the oxidation occurs under acidic conditions and involves a visually observed transient formation of a green phase, the possible oxidation routes are greatly narrowed. Under the stipulated condition of acidity the possible final products under aqueous conditions are limited to α-FeOOH (Goethite), γ-FeOOH (Lepidocrocite) and amorphous iron oxyhydroxide. The electron diffraction data does not identify Lepidocrocite as being present, but does allow the possibility of Goethite. Amorphous iron oxyhydroxide, by its very nature, would not give an identifiable diffraction pattern. The proposed mechanism of formation of Goethite under acidic conditions can also involve the intermediate formation of a green complex (35):

\[ \text{[Fe(II) O}_x \text{Fe(III)}_3]^{(11-2x)+} \]

These green complexes can, in the presence of anions such as
Cl\(^-\) and SO\(_4\)^{2-}\), be precipitated as green rust - identified as green rust I in the diffraction table. Examination of the information contained in Table 2 thus shows that the observed diffraction data may be satisfied by postulating the existence of green rust I and Goethite in the interfacial zone, a combination consistent with the known conditions of formation.

Similarly, the EDX analysis can be interpreted on the basis of this supposition:

Region I of high Fe concentration found on samples of least attack can be regarded as residual iron, presumably oxidised slightly as a result of storage in air. Electron diffraction patterns could be obtained from this region, which suggested a great deal of amorphous character to this region indicated by the diffuse nature of the diffraction patterns.

Region III shows an Fe:O ratio of ~ 4:5, suggestive of the compound FeO. This was supported by the data for Figure 22 which was found to have a diffraction pattern consisting solely of FeO (Wustite) reflections. This particular region was found in very small quantities in only a few areas on samples of intermediate attack. It is , therefore, proposed that these areas are the residual areas of iron remaining once the Haloflex has dried, which after microtoming have transformed completely to FeO. It should be noted that, from equilibrium thermodynamic considerations, the formation of bulk Wustite should not occur below 500°C. However, it is still unclear as to whether small clusters of Wustite can be formed in very thin interfacial layers at room temperature, or indeed, by the decay of Fe(OH)\(_2\) in conditions of limited O\(_2\) access (29).
It is worthy of note that there is good general agreement between Fe/O ratios proposed by electron diffraction and EDX, indicating that the K-factor used for oxygen in this situation can be considered fairly accurate. The over estimation of O content by EDX is accounted for by contamination with oxygen containing oils etc. in the microscope column which are cracked on the specimen surface by the electron beam.

Region II (Figure 22), present on samples of least attack, can be considered to be the initial stages of interfacial zone formation, where acidic dissolution of the iron has led to the formation of some oxide or oxyhydroxide. This particular micrograph has been taken under conditions where objective lens apertures have been inserted to improve diffraction contrast of the image. EDX necessitates the removal of these apertures to avoid the spurious X-ray signal (of copper) that they generate. A great deal of contrast is therefore lost on the viewed image for EDX analysis and, in particular, the lighter regions of Figure 22 disappear altogether. In order to be certain of taking an analysis from this oxide region it is necessary to focus the electron beam onto one of the darker regions of oxide so that specimen drift can be easily corrected during spectral acquisition by constantly moving the beam back onto a recognisable feature in the region of interest. The EDX analysis can therefore be assumed to be taken from an area of higher Fe content (Fe has a much higher mass contrast than O), and it is expected that the proximity of the residual iron will result in an increased Fe signal due to beam spreading into this region. However, the recorded Fe/O ratio of ~1:2 is what we would expect from the
formation of Goethite and green rust I. Electron diffraction data for this region also supports the assumption that these two compounds are present. It can only be assumed that, in this case, the increased Fe signal described and the enhanced O signal due to contamination and polymer degradation simply cancel each other out.

Region IV (Figure 22) is present as the predominant interfacial feature on the samples of intermediate attack. Again EDX analysis was performed without objective lens apertures, which reduce contrast, but in this case the interfacial layer was considerably wider (up to ~0.4μm) so that an electron beam could be allowed to drift around the specimen without leaving the region of interest. The resulting Fe/O ratio in this case was 1:5, which initially seems very high. The observed high O content can be explained by the fact that the growing interfacial layer is not likely to be completely oxide in composition. It is quite likely that areas of polymer have been trapped in the growing interface leading to a higher O signal. Also, beam spreading is likely to cause an enhanced O signal since the interfacial zone in this case is bounded by polymeric material on both sides (resin and binder). The electron path length in these materials is likely to be high resulting in an X-ray signal generated from a larger than expected analysed volume (Figure 33). Electron diffraction in this area gave patterns consistent with this region being a mixture of green rust I and Goethite.

Samples microtomed from areas of maximum attack had no interfacial areas and the dispersed phase present around the latex cells did not yield diffraction patterns. It could be supposed
TEM specimen

e beam

X-rays to analyser

analysed volume

Interaction volume in an analysed interface by TEM and EDX

Figure 33 Analysis volume in TEM specimens.
that this phase, brown in appearance, would be the final transformation product Goethite. This is supported by the fact that, on control specimens which have not had microtome samples removed from them, the black region on the slides has been observed to transform completely to the brown coloured phase over a period of time (~2-6 months on various specimens). It is expected that green rust I would transform to Goethite under exposed conditions. Further support for this mechanism can be found in the other technique used. X-ray mapping has shown chlorine to be associated with the interfacial layer; this has been confirmed by RBS, thereby removing any doubt that the chlorine X-ray signal enhancement could be an artefact due to fluorescence by iron. EDX also showed this chlorine concentration to be very low indeed (in the range ~1-4%), which would suggest that no bulk chloride had formed.

The XPS analysis again supports the inclusion of chlorine in the interfacial oxide from the depth profile analysis. The chemical state information, obtained from these profiles is, however, not so clear. The normal interpretation of the mixed states of iron being present in the interface, as evidenced by the growth of a shoulder on the Fe2p peak, may be invalid in this series of etch. The effect of an energetic argon ion beam is not sufficiently understood to clearly state whether ion beam reduction (105) is occurring or not, particularly in cases where an energetic beam is incident on a thermally insulating material (i.e. a polymer) whereby localised surface heating is apparent.

It is therefore necessary to investigate the reductive effect
of the argon beam on our thin polymer films to assess the validity of a mixed valence iron oxide being identified.

This investigation was pursued by the removal of the Haloflex film coating by solvent elution using N-methyl-pyrrolidone. The elution was performed in a glove box under an inert nitrogen atmosphere in order to prevent oxidation of the exposed interfacial layer prior to analysis. It must be noted that the Haloflex coating adheres very strongly to the interface and therefore could not be completely removed even under repeated washing with the strongly eluting N methyl-pyrrolidone.

Figure 34 shows the change in Fe2p peaks on argon etching. Figure 34a shows the Fe2p peaks to be mainly trivalent prior to etching which quickly becomes divalent, Figure 34b, and eventually a mixture of metallic and divalent, Figure 34c, after only 12 minutes etching. Whereas it is not inconceivable that so thin a layer of oxide is left on the metal surface such that only 12 minutes etching expose the metallic substrate beneath, it does not seem very likely. If the etch rate of Fakes et al. (75) of 3.5nm/minute for a mixed oxide/polymeric material may be taken as a guide for our system, this would mean the interface oxide present being of the order of 42nm which would contradict micrographs of interfacial areas presented in this (and later) Chapter(s) i.e. the interfacial oxide thickness in Figure 20 is of the order of 500nm. Therefore, whilst still not precluding the possibility of a 'real' effect causing the appearance of a divalent and metallic Fe2p peak in XPS spectra, it is proposed that this is largely (although not entirely) an artefact of ion
Figure 34 Ion beam reduction of iron
beam reduction. The main consequence of this proposal is that interpretation of chemical state information from acquired spectra is essentially impossible. It is for this reason that no deconvolution of Fe2p peaks into constituent valence states has been undertaken.

The different analyses have thus proposed that an iron oxide containing a small amount of chloride exists at the polymer metal interface. The diffraction analysis has proposed this oxide to be comprised of green rust I and α-FeOOH, which is supported by observed colour transformations in the drying and dried interface. XPS definitely does not contradict but, perhaps, affirms the mixed valence state of the interface oxide.

The evidence, therefore, suggests:-

The attack of the acidic Haloflex binder on an iron substrate, after initial etch of the surface, results in an interfacial film of mixed oxides and hydroxides. Initial oxidation of the iron produces a green complex which in the presence of chloride ions in the coating is precipitated as green rust. Further oxidation causes green rust to transform to Goethite which gives a characteristic brown colouration. It must also be noted that the corrosion product surrounding the prior latex particles observed in most of the interfacial micrographs in this chapter has not been identified, due to its existence in extremely thin layers. EDX has shown these outlines to be iron and chlorine rich. This, therefore, allows the possibility of such outlining to also be a green rust or, indeed, to have the potential to become a site for green rust formation. This factor will form the basis of Chapter
4, where ionic pigment additions are introduced into Haloflex in an attempt to utilise the iron corrosion product to form a beneficial anti-corrosive protective layer around the interface and latex particles.

The evaporated iron film and thin unpigmented coating produce an accelerated oxidation process, which on the wedge-shape coating developed for this work, shows the sequential build up of the film, as depicted schematically in Figure 35.

Comment must be made on the proposed reaction route in the context of previous work on oxidation of iron in mildly acidic/neutral solutions. The series of papers by McEnaney and Smith (24-26) indicate green rust as an intermediary for $\gamma$-FeOOH and present electron diffraction data (77) of the green rust formed. The recorded interplanar spacing of $\sim 7.5\text{Å}$ is much larger than the 7.1Å spacing recorded in our work and thus indicates that a different green rust, as well as final oxidation product, is formed. However, Butler and Beynon (27) in presenting an investigation on the corrosion of mild steel in boiling molar magnesium chloride indicate the formation of $\alpha$-FeOOH and further identify green rust as an intermediary in less concentrated chloride solutions. Their electron diffraction data is worthy of note when compared to an amended form of our data where the reflections corresponding to green rust and not $\alpha$-FeOOH (i.e. no coincidence between the two) are assigned as being the only green rust reflections.
Figure 35  The schematic sequential dissolution of iron coated with Haloflex.
<table>
<thead>
<tr>
<th>Butler, Beynon</th>
<th>Our work</th>
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<tbody>
<tr>
<td>d spacing Å</td>
<td>d spacing Å</td>
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<tr>
<td>7.14</td>
<td>7.10</td>
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<tr>
<td>3.55</td>
<td>3.55</td>
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<td>2.714</td>
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<td>2.226</td>
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<td>1.508</td>
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<td>1.460</td>
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It can, therefore, be assumed that these green rusts are of similar nature. Our results may also be explained in terms of the work of Butler and Beynon by taking into account the time dependence of oxidation conditions in the coating/metal system. As the Haloflex coating dries, the chloride solution adjacent to the corroding metal will become more concentrated thereby changing the oxidation route. The interface would then consist of green rust and α-FeOOH as proposed.
The analysis of Chapter 3 has established the existence (at least in part) of green rust I at the interface between Haloflex and iron. The stability and formation of green rust according to Detournay et al. (38) defines the pH range of its existence to be between slightly alkaline/slightly acidic. The analysis of Chapter 3 involved specimens buffered to ~pH 5.5 which subsequently yielded green rust in the interface, enabling the use of this value as a pH 'marker' for definite green rust formation. This value must, therefore, be viewed in terms of research carried out by Lewis (78), who analysed pH vs. time variations in the drying of Haloflex paint films, of composition identical to those used in this study, when laid down on glass panels (Figure 36). These plots show that as Haloflex dries it becomes more acidic due to loss of water and residual ammonia (present as an artefact of the latex polymerisation process). This decrease in pH is likely to be countered at the polymer/metal interface when a paint is coated onto a mild steel substrate as a consequence of hydroxyl ion evolution at the cathode when a corrosion cell evolves. The drying paint film could thus be envisaged as consisting of an interfacial region of variable pH, but less acidic (or even alkaline) when compared to the bulk paint film. The iron dissolved at the anode surface will then be oxidised in a manner which will depend on spatial position in the film. From the arguments above we may identify two areas of different oxidation conditions, one of which — the interface — providing an environment for green rust to form, but the other — the bulk paint film — in which further mineralisation of the latex particles may
Variation of paint pH with time on glass

Figure 36 pH variations in Haloflex coatings applied to glass panels. (After (78)).
occur. The latter process gives the bulk paint the potential to display an enhanced rôle in anti-corrosion since the network of prior latex particle surface may become an inter-connected anion exchange matrix.

The micrographs of the sectioned interfaces shown in Chapter 3 (Figure 35) clearly show the latex cells of the Haloflex to be outlined. EDX analysis has shown these outlines to be of iron dissolved from the substrate. It is proposed that iron dissolved in such a manner is carried by convection currents in the drying aqueous phase of the paint and distributed through the latex. It is intended to establish the merit of this proposal by the observation of outlined cells in a fully sectioned paint film. The mechanism of convection is likely to distribute the divalent Fe$^{2+}$ ion through the film with such a speed that significant oxidation to the trivalent Fe$^{3+}$ ion occurs only near the polymer/air interface. Under these conditions within the paint film it thus seems unlikely that the necessary conditions for green rust formation are satisfied, namely the coexistence of Fe$^{2+}$ and Fe$^{3+}$, a limited O$_2$ supply and an only slightly acidic pH. However, as stated previously, green rust is one single member of the larger pyroaurite family of compounds, wherein variations of composition and conditions of formation exist. It is therefore our intention to attempt to create, by pigment or ionic additions, a pyroaurite-type compound in the paint film to provide a possible network of anion exchange through the bulk of the polymer film. It may also be possible to achieve, by pigmentation, an enhancement of this interfacial pyroaurite by the alleviation of the need for the coexistence of Fe$^{3+}$ and Fe$^{2+}$ under suitable
conditions. The aim of such a pigment addition philosophy is to provide a suitable alternative trivalent ion to be freely available in the polymer film in order to combine with divalent Fe\(^{2+}\) and likewise an alternative divalent ion to combine with Fe\(^{3+}\).

The pigments chosen for addition into Haloflex were magnesium, added as magnesium chloride MgCl\(_2\), and aluminium, added as aluminium sulphate Al\(_2\)(SO\(_4\))\(_3\). Both cations are known to be able to form a pyroaurite-type compound with iron. A further pigment addition examined was that of hydrotalcite Mg\(_6\)Al\(_2\)(OH)\(_{16}\)(CO\(_3\))\(_4\)H\(_2\)O, which is itself a member of the pyroaurite family. If stable in Haloflex, this would provide a further anion exchange pigment.


The analytical electron microscopy study of the pigmented films was undertaken to identify the interaction of an added species or pigment with the Haloflex/iron system. Identification of artefacts due solely to the interaction with iron has been achieved by the study of Haloflex films laid down on glass plates. The subsequent pigmented Haloflex paint reactions with the iron substrate have been studied by applying the Haloflex paint to an evaporated iron film in an attempt to obtain a whole interface in cross-section and also to mild-steel Q-panels which, although not revealing a full interface to study from microtomy considerations, will nevertheless provide a 'real' substrate of commercial mild steel in a cold rolled condition.

The following pigment solutions were added to a Haloflex paint:

(i) Aluminium Sulphate $\text{Al}_2(\text{SO}_4)_3$ 0.1 Molar*
(ii) Magnesium Chloride $\text{MgCl}_2$ 1 Molar*
(iii) Hydrotalcite $\text{Mg}_6\text{Al}_2(\text{OH})_16(\text{CO}_3).4\text{H}_2\text{O}$.

made by alkali additions (NaOH) to a mixed solution of 0.1 molar magnesium and aluminium sulphates in a ratio of 3:1.

* concentrations are based on near solubility limit.

A 20% by volume addition of pigment solution (called PVC - pigment volume concentration - in the paint industry) was used in the formulated paint, on the basis of being able to observe pigment interaction rather than on grounds of paint technology. It is realised that such a large addition may be detrimental to the barrier properties of the paint film by causing incomplete coalescence of the latex film.

N.B. It must also be borne in mind that a Haloflex formulated paint is acidic (pH 5-6) and has an aqueous phase containing 0.1 molar hydrogen chloride and 0.02 molar sodium sulphate (ICI ref. data).

The substrate materials for the pigmented paint additions were either glass panels (for reference purposes), evaporated iron films or degreased and abraded mild-steel Q-panels.

Sections were removed from the glass panels and evaporated
iron films by simple incision and peeling using scalpel and tweezers.

Coated Q-panels were treated in the iodine stripping rig described in section 3.2.1. Metal dissolved films were then embedded in resin and, in common with the sections prepared by other means, were microtomed for TEM analysis.

A distinction is made in the following text between the terms Haloflex binder and Haloflex paint. Haloflex binder refers to the Haloflex 202S aqueous latex dispersion with only subsequent additions of a buffering agent (alkaline potassium hydrogen phthalate). Haloflex paint refers to a formulation given in Appendix 1, whereby subsequent additions of thickening pigments, defoamer etc. have been added to give the properties of a commercial paint.

4.1.2. Paints Laid-Down on Glass Plates.

Figure 37 shows sections of paint without the further additions of Mg or Al. Figure 37a shows a large area of fully coalesced latex and Figure 37b shows an area of inhomogeniety in the film around the pigments of the base paint - in this case barytes ($\text{BaS}_2$). No outlining of the prior latex cells could be detected in these films.

Figures 38 and 39 show the aluminium (III) and magnesium (II) pigmented paint sections laid-down on glass plates. The magnesium sectioned paint shows no latex cell decoration although there are indications of incomplete latex coalescence when compared to Figure 37, the paint without Mg(II) or Al(III)
Figure 37 Haloflex paint without further ionic additions
a) fully coalesced paint   b) areas of inhomogeneity around barytes pigment.
Figure 38  Aluminium (III) pigmented paint coated on a glass panel.

Figure 39  Magnesium (II) pigmented paint coated on a glass panel.
additions. This Mg(II) pigmented paint was also very brittle - flaking when cut by the scalpel. It can thus be inferred that Mg(II) additions interfere with the particle coalescence in the paint - probably by ionic interaction with the latex stabilising surfactant. The aluminium (III)pigmented paint, shows a different interaction with the prior latex particles. In this case voids have appeared in a number of cases around particles - perhaps indicating that whatever decorated the latex particles simply fell out during or following the preparation of the electron transparent specimens. The Al(III)pigmented films, however, displayed the mechanical properties of a normal Haloflex paint film.

In both cases of pigmented films laid-down on glass, the presence of the added pigment could not be detected by EDX analysis.

4.1.3. Paint Films Laid-Down on Evaporated Iron.

In general, the sections microtomed from the paint films laid-down on evaporated iron were a very poor quality. Detachment of polymer from the iron substrate was observed in all cases and, more importantly, the paint films themselves were generally shredded by the microtome procedure, leaving scattered remnants of paint sections to be examined. It was therefore decided in a number of cases that a pigmented binder (not the paint in Appendix 1) on iron would be studied in an attempt to alleviate the damage caused to the polymer film when microtoming through the hard pigments of the paint (TiO₂, barytes etc.). From this study,
various salient features could be ascertained from the largely destroyed cross-sections. However, some of the sections of MgCl$_2$ pigmented paint yielded several usable cross-sectional areas. The results of this analysis are presented below.

Figure 40 shows the effect of the binder attack on an iron substrate. A homogeneous distribution of iron through the film to the polymer/air interface is observed. Although not conclusive, it appears that the prior latex particles at the polymer/metal and polymer/air interfaces appear to be slightly more heavily outlined than those in the bulk of the polymer film.

Figure 41 shows the hydrotalcite pigmented binder on evaporated iron. Here, most of the polymer/metal interfacial structure has been lost with the interface easily being identified by a series of voids. The most important features of this section are firstly that large precipitated areas of alumina Al$_2$O$_3$ (Figure 42) can be detected in the film (by EDX) and secondly, there is a noticeable polymer/air interfacial structure developed (Figure 43). EDX performed in this area detected the presence of magnesium and iron. No sections could be obtained with a hydrotalcite pigmented paint and poor choice of microtome resin for the sections presented is evident by the noticeable polymer swelling of the film. (The resin used in this case was not used in further studies). Complementary studies on the Mg(II) and Al(III) pigmented systems were considered to yield sufficient data on the effects noted in these sections due to the apparent dissociation of the hydrotalcite into its constituent oxides/hydroxides.

Figure 44 shows the section of an aluminium (III) pigmented binder. The film can be observed to contain a large number of
Figure 40 Haloflex binder on iron.

Figure 41 Hydrotalcite pigmented binder on iron.
Figure 42 Areas of alumina in hydrotalcite pigmented binder.

Figure 43 Polymer/air interface in hydrotalcite pigmented binder.
Figure 44 Aluminium (III) pigmented binder on iron. Note large number of voids (white areas).

Figure 45 Magnesium (II) pigmented paint on iron. Note outlined cells at both polymer/air and polymer/metal interfaces.
voids (white areas). No intact polymer/metal interfacial areas could be observed in these films and no presence of aluminium could be detected. It appears that any compound formation occurring in this film is detached from the film during microtomy. Further investigation of aluminium modified binder on evaporated iron was deemed unnecessary in the light of the later investigation on Q-panels (described in section 4.1.4. below).

Figure 45 shows the magnesium (II) pigmented paint on evaporated iron - here it was possible to use the pigmented paint rather than the binder for the study. Figure 45 shows the complete film through thickness and illustrates the proposed mechanism of convection of dissolved iron through the Haloflex film. The polymer/metal and polymer/air interfaces both show outlined latex cells, whilst the bulk of the film does not. Figure 46, showing the polymer/metal interface in greater detail, shows no large scale interfacial compound is formed. Indeed, in a number of areas (Figure 47) a swelling of the interface was observed. These swollen but featureless areas around the interface were found to contain magnesium. Elsewhere, the presence of magnesium could not be confirmed by EDX.

The examination of pigmented Haloflex on evaporated iron was largely hindered by the interfacial structure and pigment/film interaction being destroyed by the microtome procedure. The features identified in this analysis are, on the whole, very similar to those observed in the analysis of Haloflex on Q-panels and will therefore be discussed following the presentation of those results and the results of a complementary XPS analysis.
Figure 46  Magnesium (II) pigmented paint on iron. Polymer/metal interface.

Figure 47  Magnesium (II) pigmented paint on iron. Swelling of polymer/metal interface region.
4.1.4. Paint Films Laid-Down on Mild Steel Panels

For this study paint was applied to mild steel Q-panels as a single coat. The iodine/methanol mixture (see sect. 3.2.1.) was subsequently employed to produce polymer/oxide films by dissolution of the mild steel substrate. Once again the sections produced by microtomy were largely damaged, but did produce useful features for investigation.

Figure 48 shows sections taken from the aluminium pigmented paint. Figure 48a shows the polymer metal region to be very heavily outlined with evident large-scale localised substrate attack. Figure 49 shows an enlarged area of this interface with the corresponding electron diffraction pattern obtained in one of the dark interfacial areas being shown as Figure 50. The diffuse nature of the diffracted disc prevents accurate determination of the interplanar d spacing giving rise to this diffraction, but can be estimated to be in the region of 7-8Å. EDX analysis (Figure 51) of this area also shows it to be enriched in aluminium. Figure 48b shows the polymer/air interface to be comprised of lightly outlined latex cells amongst the barytes pigment particles. No enrichment in aluminium could be detected in this region by EDX.

Figure 52 shows the sections taken from the magnesium pigmented paint. Figure 52a shows the polymer/metal interface with heavily outlined latex cells as in the case of aluminium. Figure 52b shows an electron diffraction pattern obtained from this interfacial area. Again an estimated d-spacing of 7-8Å can be attributed with the diffracted disc. EDX analysis could not detect the presence of magnesium in this region. Figures 53 and 54 show...
Figure 48 Aluminium (III) pigmented paint on Q-panel.

a) Polymer/metal interface  b) polymer/air interface.
Figure 49  Aluminium (III) pigmented paint on Q-panel. Polymer/metal interface area giving rise to diffraction discs of Figure 50.

Figure 50  Convergent beam electron diffraction in dark areas of Figure 49.
Figure 51. EDX spectrum corresponding to dark areas of Figure 49.
Figure 52  Magnesium (II) pigmented paint on Q-panel.
a) Polymer/metal interface  b) electron diffraction pattern from (a).
Figure 53 Magnesium (II) pigmented paint on Q-panel. Polymer/air interface.

Figure 54 As for Figure 53. Higher magnification.
the polymer/air interface in the magnesium pigmented Haloflex paint. The formation of an interfacial layer is very evident. EDX analysis of this polymer/air interface detected the presence of magnesium in this region (Figure 55).

4.2. XPS Analysis of Pigmented Films.

XPS analysis was performed on pigmented paint coated on mild steel Q-panels, which were subsequently etched in iodine/methanol solution to reveal the interfacial oxide. The Haloflex coating was applied by a blade coater to give a two-coat thickness of approximately 60μm. After drying and allowance for continuing coalescing reactions in the latex for a minimum of 9 days, the mild steel coupons were etched before being introduced into the XPS spectrometer as described in sect.3.2.1.

4.2.1 Depth Profile Analysis.

The depth profiles for the pigmented paints are shown as Figures 56-58.

Figure 56 shows the depth profile obtained for a hydrotalcite pigmented paint on mild steel. Observation of the trends in the respective concentrations show that, as expected, the iron and oxygen curves, apart from an anomaly at t=14mins, are essentially in-phase. Closer examination also reveals that the variations in the iron curve are largely matched by those of both the magnesium and chlorine, perhaps suggesting an agglomeration of the four elements Fe, O, Cl and Mg. Aluminium could not be detected in the analysed sections at all.
Figure 55 EDX spectrum for Figure 54.
DEPTH PROFILE FOR A HYDROTALCITE
PIGMENTED HALOFLEX ON STEEL

ATOMIC CONCENTRATION %

ETCH TIME (MINUTES)
DEPTH PROFILE FOR AN ALUMINIUM PIGMENTED HALOFLEX

ATOMIC CONCENTRATION %

ETCH TIME (MINUTES)
Figure 57 shows the depth profile for a magnesium pigmented paint. The suggestion that Fe, O, Mg and Cl are associated is reinforced by this profile. The inverse variation of these four elements compared to the polymer (carbon) phase is clearly evident indicating their association in the inorganic oxide phase.

Figure 58 shows the final depth profile; that of the aluminium pigmented paint. The variation of aluminium concentration when compared to that of iron would seem to suggest that these elements are not associated. However, it must be noted that over the depth profiled, Fe and Al exist in two distinct regions with Fe:Al ratios of ~3:1 and ~9:1. The curve for chlorine also tends to vary with that of aluminium. Both Figure 57 and 58 are replotted as 57a and 58a without the carbon signal to emphasise associations.

The chemical state information available in the depth profiled samples has again not been analysed to yield the chemical states of the elements because of the unknown extent of argon ion beam reduction on these specimens.

4.3. Discussion and Conclusions

The results presented in this chapter provide a bridge between the interpretation of the results of Chapter 3, for the studies of interfaces on evaporated iron films, with those that could be expected in real situations on mild steel. Furthermore, it is hoped to establish, with these results, the formation of synthetic pyroaurite-type compounds within a Haloflex film by pigment addition.

The sections obtained from paint films laid-down on glass
Figure 57a
Figure 58A
plates demonstrate clearly that the outlining of prior latex cells on iron or steel substrates are a direct consequence of the dissolution of iron from the coated substrate. This provides an in-situ route to obtaining a possible network of anti-corrosive pigment sites in a paint, as explained previously, by the incorporation of corrosion product and ionic additions into an ion exchange matrix. The brittleness displayed around the base pigments in an otherwise unpigmented paint indicates that the paint on its own does not readily lend itself to microtomy - a factor emphasised in the further pigmented paints where large areas of voids are present in the paint sections. The information to be gained from cross-sectional TEM does, however, far outweigh the difficulty in obtaining usable cross-sections, providing an invaluable insight into the polymer/metal interface. On simply adding aluminium (III) or magnesium (II) to the paint and coating onto a glass panel, it was possible to analyse the pigment/paint interaction in isolation from any further interaction from iron. As stated, Mg(II) was found to embrittle the Haloflex paint, suggesting some interference with coalescence i.e. the latex particle surface. It has been shown (79) that ionic species cause a flocculation of latex emulsions by creating a charge imbalance on the latex surfactant. The degree of flocculation varies with individual ionic species but is thought to be severe in the presence of di- and trivalent metal ions. By inference it could then be suggested that when Fe and Mg both interfere with the latex particle surface, coalescence will occur leaving a network of Fe and Mg coated particles. XPS analysis (Figure 57) on sections removed from mild steel Q-panels does agree with the
hypothesis of Mg and Fe association but cannot, due to ion beam reductive effects, shed any light on the chemical bonding, if any, of this Mg and Fe interaction. In the mineral form of pyroaurite containing both Mg and Fe — \( \text{Mg}_6\text{Fe}_2(\text{OH})_{16}(\text{CO}_3)\cdot4\text{H}_2\text{O} \), it is necessary for iron to exist as the trivalent \( \text{Fe}^{3+} \) species. We have proposed in the introduction to this chapter that iron, dissolved from the substrate, is initially conveyed throughout the film by convection currents in the drying aqueous phase. This was supported by the micrograph of Figure 45 (see section 4.1.3.). Therefore the existence of ferric ions would not be expected on a large scale in the oxygen deficient polymer/metal interfacial region (although it will probably exist to a minor extent), but rather in the region surrounding the polymer/air interface. It follows that the pyroaurite-type compound combining Mg and Fe is more likely to form around the polymer/air interface than it is around the polymer/metal one. This mineral formation may explain the general difficulty in detecting the presence of Mg in TEM cross-sections. As stated previously the association of Mg and Fe has been clearly demonstrated around the polymer/metal interfacial area by XPS depth analysis (Figure 57). However, EDX performed in corresponding interface regions has failed to detect the presence of Mg, yet is able to in the areas of the polymer/air interface (Figure 55).

One possible explanation for this is that the effect of the energetic focused electron beam used in EDX analysis may be to displace weakly bound atoms or molecules away from the analysed region; a thermal gradient would provide the driving force for liberated species. (In particular, polymer regions of the paint
may be observed to cross-link by electron beam interaction - evident by the drawing of surrounding polymer as densification occurs and the decrease in chlorine concentration with time). Therefore, if the magnesium surrounding the latex particles is not associated with Fe but rather weakly bound to polar surfactant, it may be liberated to diffuse away by the electron beam. In contrast, in the polymer/air interfacial regions both Mg and Fe can be readily detected existing around prior particles. Unfortunately, electron diffraction in this area has been unable to identify a pyroaurite, or indeed any other structure, as being present. Electron diffraction did present evidence (Figure 52) for the presence of a pyroaurite-type compound being present at the polymer/metal interface by an observed diffraction disc corresponding to an interplanar spacing of ~7-8Å. This disc, although very diffuse compares well with Figure 24 of Chapter 3 which is indicative of pyroaurite. EDX analysis in this region did not identify Mg as being present and therefore indicates that this interfacial film is the green rust I identified earlier. This essentially reiterates the experiments of Butler and Beynon (27) who studied the corrosion of mild steel in solutions of MgCl₂ albeit at an elevated temperature. They, too, report the formation of green rust and an associated enhanced corrosion resistance.

The addition of aluminium (III) to the Haloflex paint laid-down on glass plates was found not to interfere with the paint in the same manner as magnesium, in that the sections removed for microtomy were observed to exhibit the mechanical properties of an unpigmented Haloflex paint. Examination of these
films in cross-section reveals them to be full of voids. It can only be assumed that compounds formed from the added Al solution, being unattached by surfactant to the latex particles, simply fell out after microtomy due to lack of adhesion. The addition of aluminium (III) to a Haloflex paint and subsequent coating on mild steel did, however, indicate the presence of Al in the microtomed sections. As indicated in Figures 49 and 50 an interfacial region rich in aluminium was found to give a diffuse diffraction disc corresponding to the characteristic pyroaurite-type interplanar d-spacing of 7-8Å. The diffuse nature of this disc prevents a more accurate measurement of d-spacing. The trivalent Al\(^{3+}\) addition into the Haloflex paint was intended to combine with the divalent Fe\(^{2+}\) ferrous ion at the interface to form an interfacial film, and it appears by the observation of an aluminium containing pyroaurite that this is the case. The XPS analysis shows Al to be apparently independent of Fe concentration variation by consideration of the increase in Fe concentration and decrease in Al concentration after \(~5\) minutes etch time. However, before this change it can be observed that Fe and Al concentration curves are almost constant and are in a ratio of \(~3:1\). This is exactly the ratio that would be expected from a pyroaurite-type compound involving aluminium and iron – Fe\(_6\)Al\(_2\)(OH)\(_{16}\)(CO\(_3\))\(_4\)H\(_2\)O. The subsequent decrease in Al concentration and increase in that of iron after etching further into the oxide layer is perhaps a consequence of a different oxidation reaction of the iron. An abrupt interface is observed at this point where all analysed elements show a distinct concentration change. It is of worthy note that the iron and aluminium still remain in a fixed ratio in
this region, although why this is cannot readily be explained. It is perhaps worth speculating that this could correspond to a mixture of Fe(II)Fe(III) and FeAl pyroaurites. Studies using XPS, not associated with the depth profiling, shows aluminium to be present at the polymer/air surface. EDX does not identify this presence on TEM cross-sections – again probably due to the added pigment falling out during microtomy. It would be expected that aluminium at the polymer/air interface would form the very stable and brittle alumina, $\text{Al}_2\text{O}_3$ (but not as a continuous film).

The use of hydrotalcite, $\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)\cdot4\text{H}_2\text{O}$, as an anti-corrosive pigment in Haloflex paint must largely be discounted for the formulations under study, due to its dissociation into component oxides and hydroxides of aluminium and magnesium. Alumina, present as large precipitate particles, was identified by quantitative EDX measurements, but no investigation into the magnesium product was undertaken as it was not associated with aluminium. However, the micrographs of the hydrotalcite pigmented Haloflex binder can be considered in the light of their separate species Mg and Al, and comparisons, particularly with Mg, made. The polymer/air interface of the hydrotalcite pigmented binder shows signs of some interfacial film but also appears to contain a large number of voids. The inability to detect Mg and Al by EDX in this region could shed no further light on this film. However, from the depth profile information of Figure 56, it is clear that Mg is largely unassociated with Fe, in contrast to the case of the simply Mg pigmented paint. We can, therefore, assume that the Mg is in such a form (MgO, Mg(OH)$_2$.etc.) that it is prevented from interacting with the latex particles. The voids in TEM
cross-sections could, therefore, be assumed to be a consequence of the Al and Mg oxides/hydroxides being lost during microtomy. Thus, hydrotalcite does not seem to be a suitable anti-corrosive pigment for this paint due to dissociation in the acidic environment. Hydrotalcite may be stabilised by alkali addition (i.e. pH >~6.5), but these conditions are known to be detrimental to paint stability and so have not been employed in this study.

Conclusions

The study of pigmented Haloflex binder and paint has identified the interaction of magnesium (II) and aluminium (III) with the iron anodically dissolved from the substrate.

These pigment interactions may be summarised as:-

(1) Magnesium (II) interacts with the trivalent ferric ion deposited at the polymer/air interface by convection currents in the drying aqueous phase, to form an interfacial film of an, as yet, uncharacterised nature. The pyroaurite-type compound, green rust I, is still able to form at the polymer/metal interface of the Mg(II) pigmented Haloflex coated on mild steel.

(2) Aluminium (III) interacts with the divalent ferrous ion at the polymer/metal interface to form a pyroaurite-type compound. This interfacial film is based on the formula $\text{Fe}_6\text{Al}_2(\text{OH})_{16}(\text{CO})_3.4\text{H}_2\text{O}$, but may vary locally in composition, particularly in terms of anionic groups, where it is likely that chloride ions have been incorporated. Aluminium (III) does not interact with the polar surfactant to impair latex coalescence and appears to not readily adhere to the Haloflex paint when not bound
as a pyroaurite.

(3) Hydrotalcite is not stable in Haloflex solutions of pH ~ 5.5 and dissociates into component oxides or hydroxides, which appear to give no subsequent interaction with the paint or dissolved iron substrate i.e. it does not reflect the sum of the separate additions of Mg$^{2+}$ and Al$^{3+}$.

The formation of interfacial films at the polymer/metal and polymer/air interfaces has been demonstrated by soluble pigment addition. However, the protective nature afforded by such films has yet to be established. An investigation into the anti-corrosive ability of these pigmented Haloflex systems thus forms the basis of the following chapter, where an A.C. impedance spectroscopic study is detailed.
The investigation, so far, has established the formation of interfacial films at the polymer/metal and polymer/air interfaces in Haloflex coatings with and without ionic additions. The rôle that these films may play in the anti-corrosive ability of such coatings has, however, yet to be established. It is, therefore, the aim of this particular investigation to identify the barrier properties of pigmented Haloflex by A.C. impedance spectroscopy, whereby, at least in theory, the individual contribution of paint film and metal interface may be distinguished. This is, indeed, the main advantage of the A.C. electrochemical technique over D.C. methods, together with the 'non-destructive' nature of the A.C. technique due to the small excitation voltage, ~5mV applied, compared with typically up to 1V in D.C. measurements.

It is, perhaps, necessary to give a brief description of the experimental arrangement employed for this investigation as there is no universal arrangement employed to suit every electrode/electrolyte system.

5.1 Experimental Arrangement

On consideration of a polymer coated metal/electrode system it is generally assumed that a very small capacitance in the range $10^{-9} - 10^{-10}$ F.cm$^{-2}$ and a high resistance of the order $>>10^6$ Ωcm$^{-2}$ will be attained if the coating is protective (80, 81).
implies that the total impedance of the system to be analysed will be very high. By reference to section 2.4.3 where it is shown that a frequency response analysis measurement is made by 'balancing' the measurement system with the analysed cell impedance, it becomes clear that a very high impedance interface is needed between the analysed cell and the frequency response analyser. This is generally satisfied by circuitry involving an operational amplifier or potentiostat. Figures 59 and 60 illustrate the two experimental arrangements employed for the following investigation.

Figure 59 shows the measurement system developed at the University of Surrey by Dr J. Kajda (82), which possesses the capability of enhanced data analysis of spectra on the University PRIME mainframe computer. Figure 60 shows the Princeton Applied Research model 368 A.C. Impedance measurement system which, although possessing a more limited data processing capability, does have facilities to perform a fast Fourier Transform analysis (83) allowing higher impedances to be measured.

The essential differences between the two systems apart from these are slight and will be dealt with by explaining any deviations from ideal behaviour of A.C. response in the later discussion stage.

5.2 Experimental Procedure

A.C. impedance analysis was performed on mild steel specimens coated in an identical manner to the Q-panels in section 4.1.4
Figure 59  Schematic of A.C. impedance measurement system developed by Kajda (82).
Figure 60  Princeton Applied Research model 368 A.C. impedance measurement system.
using Haloflex containing ionic additions of either $\text{Al}_2(\text{SO}_4)_3$ or $\text{MgCl}_2$. The A.C. impedance analysis and dissolution of Q-panels to expose paint film and oxide were, in fact, performed on different areas of the same coated Q-panel.

Samples of Q-panel ~5cm in diameter were removed to fit in the test cell (Figure 61). In this cell arrangement the following conditions were employed:-

- Exposed coating: 2.5cm diameter
- Electrolyte: 3% sodium chloride
- Counter and reference electrode: platinum foil

Coated specimens were allowed at least the usual 9 days drying time before being tested. Testing was performed on samples constantly immersed in the electrolyte using the circuitry and software corresponding to Figure 59 after Kajda and, where necessary, further investigation of the high impedance behaviour using the Princeton A.C. impedance system.

In both impedance systems a 10mV A.C. ripple was generated as the excitation voltage and the coated specimen was held at the open circuit potential.

For Kajda’s system a frequency range of 100KHz to 1 Hz was scanned. The Princeton system allowed scanning from 100KHz to 2Hz using the serial scanning technique and from 4Hz-0.1Hz using the Fast Fourier Transform (FFT) routine.
Figure 61 A.C. impedance test cell.
Data output from each system was stored on floppy disk and could be plotted in the form of:-

a) Nyquist plot (real vs imaginary components of impedance i.e. $Z'$ vs $Z''$).

b) Bode plot (log frequency vs log total impedance)

and various other specialist plots for specific applications.

5.3 Results

5.3.1. Aluminium Sulphate Pigmented Haloflex

The impedance data for the Al coated Haloflex (coating = 2 coats giving dry thickness of ~60μm) is first presented as Nyquist plots (Figures 62 and 63) and described in terms of initial impedance loss on immersion and subsequent recovery with time. Corresponding Bode plots are presented as Figures 64 and 65.

From these plots it is important to note the shape of the Nyquist semi-circles in comparison to the ideal plots shown in section 2.4.4.1. The depressed semi-circles (note the X and Y scales are not equal) suggest non-ideal behaviour and even the possibility of a second Nyquist semi-circle due to multiple components existing in the coating. (This apparent discrepancy will be discussed at a later stage). The Bode plots, however, show behaviour consistent with that described in the earlier section 2.4.4.2.

Tabulated values of coating capacitance $C_d$, electrolytic
Figure 62: Nyquist plot showing impedance drop of Al coating on immersion in 3% NaCl solution.
Figure 63

NYQUIST PLOT FOR STAGES OF AL COATING "RECOVERY"

- 8 DAYS
- 15 DAYS
- 21 DAYS

- IMAGINARY COMPONENT OF IMPEDANCE (OHMS) $\times 10^3$
- REAL COMPONENT OF IMPEDANCE (OHMS) $\times 10^3$
Figure 64: Bode plots for Haloflex+Al immersed in NaCl.

- Log total impedance (Ohms) vs. log frequency (Hz).
- X10^-1 scale.
- Two plots indicating changes over time in NaCl.
- On immersion.
- 4 hours.
Figure 65

BODE PLOTS FOR HALOFLEX+AL IMMERSED IN NAACL

TIME IN NAACL

- 8 DAYS
- 15 DAYS
- 21 DAYS

LOG TOTAL IMPEDANCE (OHMS)

LOG FREQUENCY (HZ)

X10^-1
coating resistance $R$ and interfacial resistance $R_p$ are given as Table 3. $R_p$ and $R$ are estimated from Nyquist data. $C_{di}$ is estimated from extrapolation of the linear part of the Bode plot (see section 2.4.4).

5.3.2. Magnesium Chloride Pigmented Haloflex

Representative plots of the MgCl₂ pigmented Haloflex immersed in NaCl (2 coats to give a dry coat thickness of ~120μm) are shown as Figures 66-67. As is evident from these plots penetration of electrolyte to the underlying substrate has not occurred even after 42 days immersion; the resultant plots showing a capacitive coating behaviour.

5.3.3 Discussion of Impedance Plots

The behaviour of the ionic pigmented coatings must initially be compared with the reported impedance behaviour of a Haloflex paint investigated by ICI plc. (16). The impedance behaviour presented as Figure 68, is described in terms of decreasing resistance and increasing capacitance of the paint film for the first 9 days exposure. After this period, the coating began to recover its protective properties i.e. increasing resistance and decreasing film capacitance. This behaviour is explained in terms of initial film resistance decrease followed by corrosive attack of the substrate. The coating recovery was associated with the underfilm darkening phenomena at the coating/metal interface and
Variation in electrochemical coating parameters for Haloflex + aluminium sulphate immersed in 3% NaCl

<table>
<thead>
<tr>
<th>Immersion time</th>
<th>$C_{d1}$ ($F cm^{-1}10^{-6}$)</th>
<th>$R_p$ (KΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>On immersion</td>
<td>0.1556</td>
<td>62.9</td>
</tr>
<tr>
<td>4 hours</td>
<td>2.82</td>
<td>7.9</td>
</tr>
<tr>
<td>8 days</td>
<td>0.788</td>
<td>36.2</td>
</tr>
<tr>
<td>15 days</td>
<td>0.346</td>
<td>79.2</td>
</tr>
<tr>
<td>21 days</td>
<td>0.224</td>
<td>112.0</td>
</tr>
</tbody>
</table>

Table 3.
Figure 66

$10^3$ NYQUIST PLOTS SHOWING RESPONSE OF HALOFLEX+MG IN NAACL

IMAGINARY COMPONENT OF IMPEDANCE (OHMS)

REAL COMPONENT OF IMPEDANCE (OHMS) $\times 10^3$

TIME IN NAACL
1 DAY
42 DAYS
Figure 67
Figure 68 Nyquist plots for Haloflex in 3% NaCl. After Padget and Moreland (16).
attributed to the formation of a protective interfacial compound. This recovery of protection, as indicated, by A.C. impedance was also substantiated by substrate metal loss studies, which identified this 9 day period as being of metal loss which subsequently became negligible, characteristic of the formation of the interfacial iron compounds described in Chapter 4.

The Nyquist plots presented as Figure 62 raise a number of questions if an ideal electrical equivalent circuit is proposed for this coated system. Most proposed equivalent circuits of polymer coated metals are based on the model of Figure 69 after (84), where an interface term is incorporated i.e. \( C_c \) and \( R_{po} \) refer to the polymer and \( C_{dl} \) and \( R_p \) refer to capacitance of the double layer and ionic resistance of the polymer/metal interface. This gives rise to two Nyquist semi-circle responses due to the different characteristic relaxation time constants, \( \tau \), of the polarisation processes occurring in the polymer film and at the interface. \( \tau \) with units in seconds is given by \( \tau = R_C \). However, the resultant Nyquist plot will only display this two semi-circle behaviour if the characteristic time constants involved are substantially different. A 'ball park' figure of such constants differing by a factor \( \tau_1/\tau_2 > 20 \) was given by Walter (85) as a prerequisite for visual separation of semi-circles. It can, therefore, be assumed that if a system, where an obvious interface reaction is occurring (such as the underfilm darkening in Haloflex), displays an apparent single semi-circular behaviour, then the characteristic relaxation times for interface and polymer polarisation processes are similar. This concept is illustrated.
Figure 69 Equivalent circuit for a polymer coated metal. After (84).
as Figure 70.

The Nyquist plots for our investigation of an $\text{Al}_2(\text{SO}_4)_3$ pigmented Haloflex also appear as distorted semi-circles and follow a very similar trend of initial coating protection loss followed by a recovery and, indeed, enhancement of protective properties as both capacitance and interface charge transfer resistance increase; $R_p$ to a higher than initial value. It could, therefore, be suggested that a similar protective interface was being formed in both cases of 'normal' Haloflex and that pigmented with $\text{Al}^{3+}$ ionic additions.

The series of Nyquist plots can be interpreted in terms of a poorly prepared paint film with an interfacial film formation. On immersion (Figure 62), rapid uptake of electrolyte is evident by the formation of a semi-circle (therefore not capacitive) and low frequency loop, which has been attributed by various sources as a contribution by an inductive component (86, 87) or a second semi-circle due to another capacitance component. After 4 hours immersion significant substrate corrosion is evident by the loss of coating protection properties indicated by substantial diffusion occurring through the film by a diffusion 'tail' at lower frequencies. This tail becomes less pronounced as coating properties recover (Figure 63), thus indicating a reduction in underfilm corrosion.

The Bode plots for the Al(III) pigmented Haloflex can be interpreted in a similar manner, where the low frequency plateau region of the plot shows a slight gradient; the degree of which indicating extent of diffusion processes (88).
Figure 70 Effect of varying time constant ratio $\tau_1/\tau_2$ in a two time constant system. $\tau_1 = \text{constant} = 0.5134$. 

Coating resistance of 1 Gohm

Coating resistance of 100 Mohms

Coating resistance of 10 Mohms
The Bode and Nyquist plots for magnesium pigmented Haloflex (Figures 66 and 67) are clear in that they show the coating to be capacitive i.e. electrolyte has not penetrated to the substrate after 42 days immersion in 3% NaCl. The capacitive behaviour investigated necessitated the use of the Princeton fast fourier transform routine for frequency response analysis. This enabled the analysis of lower frequency points to identify any 'tailing off' of capacitive behaviour, but this was not observed. A fast fourier transform is necessary in analysing low frequency response because of the simultaneous application of all frequency signals leading to the experiment time being that of the longest i.e. 0.01Hz = 100 second waveform. This not only allows experiments to be completed in a considerably shorter time than serial frequency response, but also means that the applied voltage is held for less total time, thereby reducing irreversible polarisation processes if present.

The addition of the pigments to a Haloflex paint can therefore be summised as follows:

i) Addition of Al$^{3+}$ to Haloflex results in similar behaviour to 'normal' Haloflex paints on mild steel. An interfacial reaction causes an enhancement of anti-corrosive properties of the paint after an initial period of substrate attack. The addition of Al(III) has not been proven to enhance the underfilm darkening reaction by A.C. impedance but certainly does not inhibit this possibility.
ii) Addition of the Mg$^{2+}$ into Haloflex results in a very much enhanced corrosion protection in the dry coating. Elimination of electrolyte penetration to the substrate has occurred by some reaction which will be discussed later.

Having demonstrated the protective behaviour of these pigmented paints, it is perhaps worthwhile to examine the exposed coatings to gain further insight into the interaction of pigment addition and coating. The proposed examination, in this respect, involves SEM observation of the coated specimens in cross section and XPS; of the coating surface, in the case of the Mg paint and of the metal substrate after N-methyl pyrrolidone elution of the polymer for the Al(III) coatings.

5.4 SEM Examination of A.C. Impedance Test Coatings

On removal from the 3% NaCl test solution the coated specimens were sectioned and ground down to a 1μm finish using standard metallurgical procedures. After application of a thin graphite conducting film these sections were examined using a Cambridge S250 scanning electron microscope.

5.4.1. Examination of Al$_2$(SO$_4$)$_3$ Pigmented Coating

Figure 71 shows the secondary electron image (SEI) of the coated mild steel substrate at low magnification. The blistered regions of the coating can clearly be observed as black regions
Figure 71 SEM micrograph of aluminium (III) Haloflex A.C. impedance specimen.

Figure 72 Blistered region of aluminium (III) Haloflex polymer/metal interface.
against the bright featureless metal substrate (caused by high secondary electron yield of the mild steel in comparison to the coating). The corrosion product in this blistered region can be observed in the SEI as Figure 72. This friable product (evident by large voids) was indicated to be composed of Fe and O by electron probe microanalysis (EPMA). Figure 73a shows an SEI of an intact region of the coating/substrate interface where no blistering has occurred. No visible interface film formation is evident in this region, even when viewed as a back-scattered electron image (Figure 73b) (back-scattered electrons are of higher energy and come from deeper in the sample giving a mass contrast rather than topological contrast).

These two regions, intact and blistered, were later studied using XPS.

5.4.2. Examination of MgCl₂ Pigmented Coatings

Figure 74 shows the SEI micrograph for the MgCl₂ pigmented coating on steel after 42 days immersion in NaCl. The whole coating appears intact with no blistering. (Detachment of the coating at the right hand end of the micrograph is as a result of sectioning rather than blistering). A thin surface layer appears to have formed at the polymer/air interface as a uniform unbroken film. Further observation of this layer (Figure 75) revealed it to be ~20μm thick but was unable to clearly reveal a great deal of further structure (Figure 76). EPMA performed in this surface layer did reveal the presence of magnesium (Figure 77). Magnesium
Figure 73 Aluminium (III) Haloflex A.C. impedance specimen
a) SEI of intact region of polymer/metal interface
b) same but backscattered electron image.
Figure 74 Magnesium (II) Haloflex A.C. impedance specimen.

Figure 75 Magnesium (II) Haloflex A.C. impedance specimen. Polymer/air interface.
Figure 76 Magnesium (II) Haloflex A.C. impedance specimen. Polymer/air interface.
Figure 77  EPMA spectrum for region shown in Figure 76.
was not detected in any other region of the coating.

The polymer/metal interface was found to be intact for the MgCl₂ pigmented coating. This is shown as Figure 78, where a diffuse interface with no obvious interfacial reaction is observed.

SEM examination has thus revealed that for the aluminium (III) coating, interfacial corrosion has occurred causing blistering in the coating. This is in agreement with the A.C impedance spectra which showed initial rapid substrate attack followed by a recovery in properties. However, with no identification of Al so far in the coating, it is impossible to consider the rôle of the Al³⁺ in the specific area of anti-corrosive ability for this system.

The case for Mg²⁺ seems to be more clear cut. The capacitive behaviour displayed by A.C. impedance is substantiated by a completely intact polymer/metal interface. Moreover, the presence of a polymer/air film containing magnesium would tend to suggest that a barrier film is present which prevents the passage of electrolyte through the polymer coating.

A further study by XPS on the nature of this magnesium containing surface layer and an insight into the aluminium (III) coating is presented below in an attempt to gain better insight into the protection afforded by both coatings.

5.5 XPS Investigation of A.C. Impedance Specimens

An XPS investigation was performed on both Mg(II) and Al(III)
Figure 78  Magnesium (II) Haloflex A.C. impedance specimen. Polymer/metal interface.
pigmented coatings after A.C. impedance analysis.

5.5.1. XPS of the Al$_2$(SO$_4$)$_3$ Pigmented Coating

As indicated in the previous section the aluminium (III) containing coating was observed to blister after ~21 days immersion in 3% NaCl. An examination was, therefore, attempted to analyse any significant difference in interfacial character between blistered and intact regions of the metal substrate.

An area of the exposed specimen was treated with N-methyl pyrrolidone in a glove box attached to the ESCALAB under an atmosphere of flowing, oxygen-free nitrogen, to minimise oxidation before analysis. Areas under blistered and intact regions were analysed using selected area XPS (for details see Chapter 6) with a spatial resolution of ~500 µm for the larger blistered regions and ~250 µm for the intact region.

The results of this selected area comparison are presented as Figures 79-81 comparing wide scans and the narrow scans for Fe$_2$p and Al$_2$p. From Figure 79 the effect of reducing selected area can be observed clearly in that count rate is significantly reduced with increasing spatial resolution. Figure 81 shows the comparison of Al spectra and indicates the presence of Al in the areas that remained intact during the A.C. impedance tests. The Fe spectra (Figure 80) also indicate iron being in the trivalent state in the blistered region (compare satellite position with Figure 11 of Chapter 2), whereas a mixed metallic and divalent state of iron exists in the regions that have remained intact.
Figure 79  XPS on Al(III) Haloflex impedance specimens
Figure 80  XPS on Al(III) Haloflex impedance specimens
Figure 81  XPS on Al(III) Haloflex impedance specimens
It can therefore be inferred that divalent iron has combined with the aluminium in regions that have not blistered on immersion in NaCl. The corrosion protection, or non-blistering, can be attributed, therefore, to the formation of an interfacial film incorporating divalent iron (II) and aluminium (III), which provides added stability in this region.

5.5.2. XPS on MgCl₂ Pigmented Coating

XPS was performed on the polymer/air surface of MgCl₂ pigmented A.C. impedance test coatings in areas of both NaCl exposed and non-NaCl exposed test panel (i.e. w.r.t. Figure 61), the non-NaCl exposed regions exist outside the rubber seal, or gasket, in the test cell.

Figures 82 and 83 show the wide scans and Mg KLL Auger peak for these respective regions and clearly show the presence of magnesium, as indicated by the KLL Auger peak, before exposure to NaCl. After NaCl exposure Mg can not readily be detected. Note that the photoelectron peaks of Mg 1s (1305eV B.E.) and Mg 2s (90eV B.E.) cannot be used as unique identification of the presence of Mg due to their overlap with other spectral peaks; namely Fe 3s photoelectron peak and Cl LMM Auger peak at 93eV and 1304eV on a binding energy scale respectively.

The Fe2p peaks shown as Figure 84 show that on exposure to the NaCl solution the outer surface of the coating becomes enriched in iron. Note also that the iron peaks for the exposed coating appear to be mixed di- and trivalent in character. It is also
Figure 82  XPS on Mg(II) Haloflex impedance specimens
Figure 83  XPS on Mg(II) Haloflex impedance specimens
Figure 84 XPS on Mg(II) Haloflex impedance specimens
evident from the widescans that, as would be expected, Cl concentration at this surface is very much increased.

The XPS analysis of the MgCl₂ coating has thus indicated that prior to immersion in NaCl, a surface layer containing magnesium is present. By quantification analysis of elements present, Mg and Fe are found to be in a ratio of 2:1; these elements representing 3 atomic % of the analysed surface region. Following immersion in NaCl the surface is enriched in both Fe and Cl, and is found to be depleted in Mg.

5.6. Conclusions

The combined analyses of this chapter give insight into the anti-corrosive nature and interfacial film formation of Haloflex coatings with ionic additions by observing the corroding and corroded coating and relating this to interface chemistry.

It should first be reiterated that the paints used in these investigations were not designed in terms of absolute coating protection, but rather on the basis that if the ionic addition was to produce a reaction in the paint, then there was sufficient pigment present for the effect to be analysed. A large pigment volume concentration (PVC) of ~20% of the extra soluble ionic additions would, therefore, normally be considered detrimental to the paint causing incomplete coalescence of latex and hence voids in the final paint coating. Nevertheless, both Al(III) and Mg(II) pigmented coatings showed behaviour which may be considered as favourable as anti-corrosive coatings.
The Al(III) coatings, which were only 60µm in thickness, displayed rapid corrosion in the A.C. impedance tests, which may have been in part due to the aforementioned large pigment addition. However, rapid recovery of properties was evident, indicative of an interfacial film formation as is the case for a 'normal' Haloflex. Examination of the intact protected portions of the film removed from the test showed these to contain aluminium at the interface, perhaps indicating its rôle in anti-corrosive protection. What cannot be determined here is whether aluminium existed initially in the blistered regions but was dissolved as part of the anodic reaction, or that the regions that blistered were initiated from regions that did not contain aluminium. This point will be discussed in Chapter 7.

The behaviour of the Mg(II) pigmented Haloflex was found to be capacitive after 42 days immersion in 3% NaCl. For the ~110µm coating this suggests it to be far superior to reported anti-corrosive behaviour of 'normal' Haloflex coatings (18). The evidence suggests that a surface film containing both magnesium and iron is formed at the polymer/air interface which provides a barrier for the ingress of anions into the coating. The slight enrichment in iron of this surface region on exposure to NaCl has proven to be an anomaly in this respect. This may arise in a number of ways:

(i) The Mg/Fe interface film may be slowly broken down allowing a small degree of substrate corrosion. This should be reflected in break down of capacitance on A.C. impedance diagrams.

(ii) The initial Mg/Fe film not being protective but becoming so
on entry of electrolyte into the coating; Mg enhancing the formation of an Fe(II) Fe(III)/ green rust from iron existing in the near surface region. Note Fe2p spectra after NaCl exposure display di- and trivalent character. 

(iii) The Mg/Fe interface film allowing the movement of cations but not anions through the coating due to anionic exchange properties.

This point too will be discussed in Chapter 7 in the light of all investigations in this thesis.

In this respect the information obtained from XPS to date has belittled its use in gaining chemical state information. The following chapter aims to gain a fuller understanding of the interfacial films formed in our coatings by a novel XPS technique.
The concept of XPS combined with argon ion sputtering to produce a depth profile of interfaces was detailed in the analyses of Chapters 3 and 4. However, as has been demonstrated in these earlier chapters, the reductive effect of this argon sputtering has negated the ability of the XPS technique to reveal chemical state information in acquired spectra.

The pyroaurite family of compounds, and in particular green rusts, are exceptional in their formation as intermediary compounds in conditions where oxygen availability is insufficient to allow full oxidative transformation to the equilibrium end product. Having gained a knowledge of the elemental constituents associated with these green rusts it would therefore be worthwhile to attempt to establish the chemical state of these constituents as a function of position around the interface and within the coating.

A recent advance in the field of XPS, in terms of spatial resolution, combined with the development of a means of mechanically revealing the interface under UHV conditions has provided a new technique by which the interface region may be analysed with chemical state resolution. The various aspects of this new technique deserve mention in order to appreciate its relative merits in comparison with other interfacial analysis techniques.
6.1 Small Area X-ray Photoelectron Spectroscopy (SAXPS)

The traditional view of XPS is that of very high surface sensitivity (typically 3-30Å signal depth) but poor lateral resolution, typically of the order of 10mm². However, recent advances in different aspects of XPS have enabled a number of distinct methods of improving the spatial resolution of this technique to be employed. These methods are termed small (or selected) area XPS.

Figure 85 after (90) schematically shows two classes of SAXPS. These shall now briefly be mentioned.

6.1.1 Limitation of Irradiated Area

The obvious corollary to restricting the area onto which an X-ray flux is incident on a specimen is that the emitted photoelectrons are likewise restricted to this irradiated area. This can be illustrated by Figure 85a. Collimation of the X-ray beam by restricting apertures is largely unfeasible with conventional X-ray sources, due to the low flux of X-ray quanta arriving at the surface giving a correspondingly poor photoelectron emission i.e. irradiated area has decreased and photon flux density has remained constant.

Proximity of source (91) is only useful for ultra thin specimens and so is of little relevance to interfacial analyses.

Focusing by crystals (92) or other means presents a method of intensifying the X-ray flux density onto the analysed small area,
Figure 85  Two classes of selected area XPS after (90).
  a) Limitation of irradiated area.
  b) Limitation by electron optics.
thus enabling some partial recompense in photoelectron emission on reducing the irradiated area.

6.1.2 Area Selection by Electron Optical Means

Figure 85b shows the means by which the area from which photoelectrons are analysed can be selected by optical means. Collimation of the emitted photoelectron beam is performed by aperture plates at the electron analyser entrance. This is coupled with a high magnification electron transfer lens placed between the specimen and analyser (53, 54). The lens presents a linear magnification of optical signal such that, given no optical aberrations, a magnification of, for example, x10 combined with entrance aperture of (a) will give a specimen analysis diameter of a/10. Analysis diameters of the order of 250μm are obtained by this method albeit with decreased photoelectron signal intensity.

The improvement of spatial resolution in XPS is therefore achieved at the expense of photoelectron signal intensity to some degree. The microfocus X-ray source does, in practice, prevent the introduction of other standard XPS utilities i.e. ion guns, electron probe etc. into position in the analyser chamber and also is not regarded as having the same spatial resolution capabilities as the electron optical selection method. In this respect the University of Surrey instrument combines a high magnification transfer lens and variable selected area apertures in small area investigations.
With reference to Figure 85b, the University of Surrey ESCALAB Mk II has a transfer lens with magnification x3 and selected area apertures available down to a diameter of 500μm (0.5mm). In this small area mode the spatial resolution of the spectrometer has been determined by scanning a 10 keV electron beam across a silver surface and analysing the response function (95). The data recorded (Figure 86) indicates a spatial resolution of ~150μm (c.f. theoretical value 500/3 = 167μm). A spherical aberration of ~22μm in the transfer lens is also indicated as being present as 'image' resolution across a uniform feature.

The edge resolution has also been determined for the linear transfer of a 500μm silver dot on copper across the lens focus position (96) (Figure 87) in XPS. The plot of intensity vs. travel across focus position in both dispersive (perpendicular to plane of analyser hemispheres) and non dispersive (in plane of electron analyser) planes indicates that for given instrumental parameters, an edge resolution of between 112-177μm is observed. This gives a value of resolution that will be of later use in SAXPS across our interface regions.

The SAXPS conditions employed for the analyses can be summarised as follows:
- 500μm analyser entrance aperture
- transfer lens with x3 magnification
- spatial resolution ~150μm
- edge resolution ~110-180μm (by scanning a sharp edge across the analysis position).
Figure 86 Concept of spatial resolution in SAXPS.
SMALL AREA X-RAY PHOTOELECTRON SPECTROSCOPY

V. G. SCIENTIFIC ESCALAB Mk II
0.5 mm APERTURE, 3° IRIS, 100 eV PASS ENERGY
SPECIMEN: 500 μm SILVER DOT ON COPPER

NON-DISPERSIVE PLANE OF ANALYSER

\[ \Delta x = 112 \mu m \]

DISPERSIVE PLANE OF ANALYSER

\[ \Delta x = 177 \mu m \]

Figure 87 Concept of edge resolution in SAXPS.
With these resolutions in mind, it is necessary to consider the method of revealing the interfacial region between a metal and a coating of ~60-100μm coating thickness.

6.2 Milling of Polymer/Metal Taper Sections in High Vacuum

The realisation of milling polymer/metal taper sections in high vacuum has been enabled by the in house design and construction of a milling stage attachment to a V.G. ESCALAB Mk II spectrometer (97). The schematic diagram of this stage (Figure 88) shows the original proposed angled cutter for use with flat specimens. Later modifications have resulted in axis of this cutter being in the vertical plane (the samples are now tapered) and cutter drive performed by a magnetically coupled variable D.C. motor. The milling attachment, (Figure 89) when coupled to the ESCALAB preparation chamber, allows the diffusion pumps of this chamber to evacuate the previously simple rotary pumped milling stage to achieve vacuum of <10⁻⁷ torr. Interfacial oxides thus revealed are, therefore, exposed to very low partial pressures of oxygen before being analysed (typically at ~10⁻¹⁰ torr).

Other features of this stage include a liquid nitrogen reservoir for specimen cooling and thermocouple attachments for specimen temperature measurement. This readily allows the removal of a polymeric coating below the Tg of the particular polymer thereby minimising the smearing effect on milling. The depth profiling ability of taper sectioning can be illustrated
Figure 88 Schematic diagram of milling stage.
Figure 89  The milling stage constructed in the University of Surrey.
schematically by a simple diagram (Figure 90), showing how the projected cross-section of the interface is controlled by taper angle.

6.3 Experimental Procedure

Investigation of taper sections using small area XPS was performed on three coating systems:

(i) Haloflex paint (see Appendix 1) on mild steel
(ii) Haloflex + 0.1 molar Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} on mild steel
(iii) Haloflex + 1 molar MgCl\textsubscript{2} on mild steel

(Al and Mg solutions were added as 20% by volume)

Coated panels were allowed at least 9 days drying time before examination. Coupons typically 1cm\textsuperscript{2} were removed from the coated panels and glued using an epoxy resin to an XPS specimen stub. The removal by tin snips of these coupons was found to impart a very slight curvature on them, sufficient to present a grazing angle through which the specimens could be milled. This is illustrated schematically by Figure 91. Milling was performed at temperatures between -2\textdegree C to -10\textdegree C, cooling being enabled by a liquid nitrogen reservoir in the milling stage. The taper angle imparted onto the section is easily deduced knowing coating thickness (Figure 90). The analysis could therefore be performed by analysing at intervals from the bare exposed metal onto the intact polymer surface and relating chemical information to analysis depth. The point of analysis was established by
ANALYSIS DEPTH RESOLUTION IN TAPER SECTIONING

PROJECTED WIDTH OF INTERFACE = $X$
THICKNESS OF INTERFACE = $D$
ANGLE OF TAPER = $\Omega$
DEPTH $D = X \sin \Omega$

Figure 90 Schematic of lateral resolution in taper sections.
milling of angled polymer coated specimen

SCHEMATIC DIAGRAM OF MILLED SPECIMENS
alignment of cross hairs of a microscope view port to coincide with the maximum intensity of a 20μm silver spot on a copper matrix. This alignment was checked periodically allowing the relatively simple task of using a polaroid land camera to photograph the specimen and aligned cross hairs to record the XPS analysis point for each profile step.

The acquisition of XPS data in small or selected area mode requires different run parameters from the more usual general area XPS. The reduction in photoelectron signal entering into the spectrometer by aperture selection is compensated by an increase in acquisition time in order to achieve a sufficient peak definition above background. A typical acquisition time for the small area investigation of Haloflex on steel was in the region of 15 hours in total. Appendix 3 shows run parameters for both general and small area XPS for the Fe2p region. The acquisition times for small area and general area are ~4 hours 20 minutes and 33 minutes respectively. Note also that the pass energy of the analyser (CAE) is increased from 20 to 100eV for SAXPS. This increases the photoelectron signal whilst resolution (usually controlled by pass energy) is also maintained by the reduction in entrance angle of electrons into the spectrometer by the action of the entrance apertures.

The effect of such long X-ray exposure times on the polymer under investigation will be demonstrated in the next section.
6.4. Results and Discussion

6.4.1. SAXPS of Haloflex on Steel

Taper sections produced for analysis of Haloflex without further pigment additions are shown as Figure 92, where the region analysed is centred upon overlayed cross hairs. For clarity this region has been highlighted and is shown as a white dot. The Fe2p scans corresponding to Figure 92 a-f are given as Figure 93 a-f.

Observation of projected width of coating allows us to calculate degree of taper as shown in Figure 90.

i.e.

coating thickness \( \approx 80\mu m \)

projected thickness \( \approx 2.5cm \)

However, the polaroid plate has been magnified x 10, therefore from

\[
\sin \Omega = \frac{\text{Real coating thickness}}{\text{projected thickness}}
\]

\[
= \frac{80 \times 10^{-6}}{2.5 \times 10^{-3}}
\]

therefore, \( \Omega = 1.8^0 \)

Using this value of \( \Omega = 1.8^0 \) we can also calculate the analysis depth for the spectra.

i.e. from Figure 92
Figure 92 Analysis of taper sections of Haloflex on mild steel. White dot indicates centre of analysis region.
Figure 93 Fe2p scans for taper sections
<table>
<thead>
<tr>
<th>Plate</th>
<th>Observed analysis distance into coating (mm x 10)</th>
<th>Actual Depth (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>b</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>c</td>
<td>2.5</td>
<td>8</td>
</tr>
<tr>
<td>d</td>
<td>5</td>
<td>16</td>
</tr>
<tr>
<td>e</td>
<td>7</td>
<td>23</td>
</tr>
<tr>
<td>f</td>
<td>11</td>
<td>35</td>
</tr>
</tbody>
</table>

This depth profiling ability must be qualified in terms in terms of inherent spatial resolution of the SAXPS technique. With reference to section 6.1., the photoelectron signal analysed has been shown, for this experimental arrangement, to be generated from an area of ~250μm. This then gives error bars on the actual analysis depth of 250.sin 1.8° ~ 8μm.

i.e. Plate | Analysis depth into coating |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0</td>
</tr>
<tr>
<td>b</td>
<td>0 - 8μm</td>
</tr>
<tr>
<td>c</td>
<td>0 - 16μm</td>
</tr>
<tr>
<td>d</td>
<td>8 - 24μm</td>
</tr>
<tr>
<td>e</td>
<td>15 - 31μm</td>
</tr>
<tr>
<td>f</td>
<td>27 - 43μm</td>
</tr>
</tbody>
</table>

These depth regions, therefore, can profile a number of parameters through coating thickness and, in particular, allow us to establish the chemical state of the elements such as iron as it is dissolved at the substrate and taken into the coating.
Figures 94-97 show the deconvolution and peak fitting performed on an Fe2p narrow scan to analyse the constituent valence peaks present.

The peaks present are identified by numbers and are:

<table>
<thead>
<tr>
<th>Peak</th>
<th>Spin orbital</th>
<th>Valence state</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2p^{3/2}$</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>$2p^{3/2}$</td>
<td>II</td>
</tr>
<tr>
<td>3</td>
<td>$2p^{3/2}$</td>
<td>III</td>
</tr>
<tr>
<td>4</td>
<td>$2p^{3/2}$ shake-up satellite</td>
<td>II, III</td>
</tr>
<tr>
<td>5</td>
<td>$2p^{1/2}$</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>$2p^{1/2}$</td>
<td>II</td>
</tr>
<tr>
<td>7</td>
<td>$2p^{1/2}$</td>
<td>III</td>
</tr>
<tr>
<td>8</td>
<td>$2p^{1/2}$ shake-up satellite</td>
<td>II, III</td>
</tr>
</tbody>
</table>

Peak position was referenced from the work of Asami and Hashimoto (98), whereby peak separations were held constant but absolute energy values allowed to change due to effects of specimen charging. It is noted that from the work of Ke (99) the shake-up satellites should be represented by separate peaks for contributions from the II and III oxidation state. However, the peak fitting software was only able to cope with a maximum of 8 peaks and so a compromise joint peak position was employed for this procedure.

The peak fit routine was performed only on the first four scans of profile series as the final two did not have sufficient peak definition to allow peak fitting with the required degree of
Table 94. Peak fitting of Figure 92(a)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Centre (eV)</th>
<th>FWHM (eV)</th>
<th>Hght %</th>
<th>G/L %</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>80</td>
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<td>20</td>
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<td>2</td>
<td>714.6</td>
<td>3.00</td>
<td>52</td>
<td>25</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>716.4</td>
<td>3.00</td>
<td>40</td>
<td>25</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>720.0</td>
<td>6.00</td>
<td>32</td>
<td>25</td>
<td>19</td>
</tr>
<tr>
<td>5</td>
<td>725.2</td>
<td>2.50</td>
<td>37</td>
<td>31</td>
<td>9</td>
</tr>
<tr>
<td>6</td>
<td>727.4</td>
<td>3.00</td>
<td>29</td>
<td>26</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td>729.6</td>
<td>3.00</td>
<td>22</td>
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<td>8</td>
<td>734.0</td>
<td>6.00</td>
<td>17</td>
<td>28</td>
<td>10</td>
</tr>
</tbody>
</table>

100% Height (Counts) : 1881
100% Area (kceV/sec) : 0.2956
Reduced Chi Squared : 1.40
Figure 95  Peak fitting of Figure 92(b)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Centre (eV)</th>
<th>FWHM (eV)</th>
<th>Hght %</th>
<th>G/L %</th>
<th>Area %</th>
</tr>
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<tbody>
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<td>14</td>
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<tr>
<td>2</td>
<td>714.5</td>
<td>3.00</td>
<td>66</td>
<td>17</td>
<td>21</td>
</tr>
<tr>
<td>3</td>
<td>716.3</td>
<td>3.00</td>
<td>37</td>
<td>18</td>
<td>12</td>
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<tr>
<td>4</td>
<td>719.9</td>
<td>6.00</td>
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<tr>
<td>5</td>
<td>725.0</td>
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<td>24</td>
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<td>6</td>
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<td>35</td>
<td>18</td>
<td>11</td>
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<tr>
<td>7</td>
<td>729.6</td>
<td>3.00</td>
<td>23</td>
<td>19</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>733.9</td>
<td>6.00</td>
<td>13</td>
<td>19</td>
<td>8</td>
</tr>
</tbody>
</table>

100% Height (Counts) : 680
100% Area (kceV/sec) : 0.2389
Reduced Chi Squared : 0.93
Figure 9.6 Peak fitting of Figure 9.2(c)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Centre (eV)</th>
<th>FWHM (eV)</th>
<th>Hght %</th>
<th>G/L %</th>
<th>Area %</th>
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<td>3.00</td>
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<td>17</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>714.5</td>
<td>3.00</td>
<td>22</td>
<td>18</td>
<td>7</td>
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<tr>
<td>4</td>
<td>717.5</td>
<td>6.00</td>
<td>33</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>722.6</td>
<td>2.50</td>
<td>26</td>
<td>18</td>
<td>7</td>
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<tr>
<td>6</td>
<td>725.4</td>
<td>3.00</td>
<td>37</td>
<td>19</td>
<td>11</td>
</tr>
<tr>
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<td>728.1</td>
<td>3.00</td>
<td>14</td>
<td>18</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>732.4</td>
<td>6.00</td>
<td>22</td>
<td>18</td>
<td>13</td>
</tr>
</tbody>
</table>

100% Height (Counts) : 911
100% Area (keV/sec) : 0.2022
Reduced Chi Squared : 1.14
Figure 97: Peak fitting of Figure 92(d)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Centre (eV)</th>
<th>FWHM (eV)</th>
<th>Hght %</th>
<th>G/L %</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>709.4</td>
<td>2.50</td>
<td>32</td>
<td>32</td>
<td>8</td>
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<tr>
<td>2</td>
<td>712.3</td>
<td>3.00</td>
<td>83</td>
<td>32</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>714.6</td>
<td>3.00</td>
<td>33</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>717.8</td>
<td>6.00</td>
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<td>2.50</td>
<td>12</td>
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<td>3</td>
</tr>
<tr>
<td>6</td>
<td>725.2</td>
<td>3.00</td>
<td>38</td>
<td>31</td>
<td>12</td>
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<tr>
<td>7</td>
<td>728.1</td>
<td>3.00</td>
<td>23</td>
<td>22</td>
<td>7</td>
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<tr>
<td>8</td>
<td>732.4</td>
<td>6.00</td>
<td>20</td>
<td>34</td>
<td>12</td>
</tr>
</tbody>
</table>

100% Height (Counts) : 805
100% Area (kceV/sec) : 0.1646
Reduced Chi Squared : 0.89
accuracy. The peak fit was deemed 'sensible' in that the peaks in the 2p$^{3/2}$ orbital were twice as great as the corresponding peaks in the 2p$^{1/2}$ orbital.

From the percent area of each valence state identified it is interesting to note the variation in character with depth into the polymer coating i.e.

<table>
<thead>
<tr>
<th>Depth into coating</th>
<th>%Fe(0)</th>
<th>Fe(II)</th>
<th>Fe(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0µm</td>
<td>35</td>
<td>30</td>
<td>34</td>
</tr>
<tr>
<td>0-8µm</td>
<td>30</td>
<td>44</td>
<td>26</td>
</tr>
<tr>
<td>0-16µm</td>
<td>33</td>
<td>52</td>
<td>15</td>
</tr>
<tr>
<td>8-24µm</td>
<td>18</td>
<td>59</td>
<td>22</td>
</tr>
</tbody>
</table>

Analysis of this table reveals that as distance away from the polymer/metal interface increases then the divalent character of the iron becomes more dominant. Likewise, both metallic iron and divalent character decrease as the iron enters further into the polymer film. This essentially confirms our hypothesis of Chapter 4, that the nature of the polymer film and polymer/metal interface are substantially different. Hydroxyl ion evolution at the polymer/metal interface will cause a pH departure allowing an oxidation of divalent iron to the trivalent state as acidity in the region decreases. It is also interesting to note that in the region designated 0µm (polymer/metal interface) the Fe(II)/Fe(III) ratio appears to be ~1:1. This is the ratio of di- and trivalent species of iron suggested by Misawa (41) for the composition of
The SAXPS analysis has, therefore, given insight into the valence character of iron as it is taken into the Haloflex coating and also indicated a ratio of ~1:1 for Fe(II)/Fe(III) existing between the polymer and metal.

6.4.2. Haloflex with Ionic Additions on Steel

The investigation into the proposed interfacial incorporation of added ionic pigment in Haloflex coatings could not detect the presence of the added ionic species i.e. Mg(II) or Al(III), despite prolonged investigation on the revealed taper sections. Figure 98 shows the taper sections analysed. Figure 98a shows the Mg(II) Haloflex taper section before the first small area analysis. Figure 98b shows the same area immediately following this analysis and illustrates the degradation of the polymer under the photon beam. Figure 98c shows the Al(III) Haloflex taper section.

It is unclear why these sections do not reveal the added species but consideration of the extent to which the polymer/metal interface is revealed may give insight into the case for Al(III). If we use the value of $\Omega \approx 1.5^0$ for our taper section and assume an interfacial oxide of $\sim 0.5\mu\text{m}$ in thickness, then, by taper sectioning, the projected of our interface will be

$$0.5 \times 10^{-5}/\tan 1.5^0 \approx 19\mu\text{m}.$$  

Given a spatial resolution of $\approx 250\mu\text{m}$, this represents 7.6% of the analysed area.

Now, for a FeAl pyroaurite, the Fe:Al ratio is ~3:1. The XPS
Figure 98  Taper sections of Haloflex and ionic additions on mild steel.  a) Mg(II) Haloflex prior to SAXPS analysis 
b) Mg(II) Haloflex after one SAXPS analysis point 
c) Al(III) Haloflex taper section.
atomic sensitivity factor for iron is also much larger for Fe than for Al - ~x16 (100) for the respective 2p peaks. It therefore becomes apparent that it will be very difficult to detect aluminium in this section and virtually impossible if, as is likely, smearing of the milled polymer across the metal occurs. The very nature of the thin interfacial layer thus ideally requires a more shallow angle of taper and clean surface for analysis. A higher spatial resolution giving a higher proportion of the interface signal in the acquired spectrum would also be of great benefit.

The difficulty in detecting Mg(II), which we originally proposed would be predominant at the polymer/air interface, is likely to be a consequence of the gross polymer degradation encountered during the long acquisition times of the small area analysis. It is evident from Figures 98a and b that large scale cracking of the polymer surface has occurred.

To demonstrate the existence of Mg(II) and Al(III) in their respective proposed interfaces, Figure 99 shows areas of identical coated Q-panels where general area XPS has been performed. Figure 99a shows the Mg(II) Haloflex coated surface with the resulting MgKLL Auger signal shown as Figure 100d. By physically removing an Al(III) Haloflex coating from the Q-panel, an analysis was performed on the polymer/metal interface coating side (Figure 99b) and polymer/metal interface metal side (Figure 99c). The metal side of the interface was found to exhibit a weak Al signal (Figure 100a) and a corresponding predominantly divalent Fe2p peak.
(Figure 100b). The polymer side of the interface showed merely a trace of Al signal (Figure 100c).

It is therefore evident that whilst small area XPS has proved useful in observing the valence character of iron through a polymer coating, the nature of thin layers has proved more difficult to elucidate. However, the opportunity to exploit a somewhat different small area XPS technique was made available on a limited time basis and thus a further study on the aluminium (III) Haloflex is presented by ESCASCOPE imaging XPS—a method by which two dimensional XPS images of samples may be produced.

6.5. Imaging XPS of Aluminium (III) Haloflex on Steel

6.5.1. Theory of Imaging XPS

Figure 101 shows a schematic illustration of the electron optical path in a V.G. Scientific ESCASCOPE imaging spectrometer. The excitation of photoelectrons is similar to that of the ESCALAB used in the previous XPS investigations. However, the 180° hemispherical sector analyser (150° in ESCALAB) and lens system is designed to maintain the spatial relationship of the excited photoelectron on the specimen surface and at the exit plane of the analyser. A hole in the spectrum detector allows an energy filtered image in two dimensions to be recorded by a parallel charge coupled imaging detector.

The spatial resolution attainable in such a system is controlled by the width of the field of view aperture and can be less than 10μm (103). Detected images are stored in an image
Figure 101  Schematic representation of ESCASCOPE imaging XPS
framestore facility and may be later processed to allow background substraction etc.

6.5.2. Experimental Investigation

An Al(III) Haloflex paint coating as used in the SAXPS investigation was similarly tapered in the milling stage attached to the ESCALAB. The tapered section was then analysed (after inevitably being exposed to air) in a V.G. Scientific ESCASCOPE at the demonstration site of V.G. Scientific in East Grinstead, Sussex.

Image acquisition involves an initial peak position identification i.e. analogous to setting windows for peaks in STEM mapping, but further involves the setting of peak background level for later substraction. (STEM specimens do not possess background in EDX due to ultra thin section).

For our samples, individual peak images were acquired for between 20 minutes and 2 hours; performing acquisition of peak images in order of susceptibility to photon damage i.e. it is suspected that specimen heating causes degradation of the organic polymer resulting in organic chlorine loss (evolved as HCl), so this image was acquired first.

6.5.3. Results and Discussion

The acquired XPS images are shown as Figures 102 and 103. Figure 102a shows the optical image of the section. The
Figure 102 XPS images of Al(III) Haloflex on mild steel
Figure 103 XPS images of Al(III) Haloflex on mild steel
finger-like interface between the polymer (left) and metal (right) is magnified on the XPS images by x 3.5. Figure 102b shows the graduated decrease of iron concentration in this interlayer as it extends into the polymer. The aluminium (Figure 102d) likewise shows similar behaviour perhaps suggesting Fe and Al association in this interlayer. Oxygen (Figures 102c and e) is shown as metallic oxide at 531 eV (Figure 102c) and organic charge shifted oxygen at 539 eV (Figure 102e). These two Figures clearly demonstrate that this finger is an interfacial oxide of some type. Figures 103b and d showing metallic and organic chloride at 200 eV and 205 eV respectively also demonstrate that this interlayer is also enriched in chloride. Finally, Figures 103c and d show unusual behaviour in that carbon with a charge compensated nature clearly defines this interlayer finger distinct from coating and metallic substrate, and provides virtually a negative image of the organic charge shifted carbon at 291 eV. We can, by this charge compensation mechanism, assume that in this interlayer carbon is intimately mixed with a conducting oxide. An area such as the heavily outlined polymer/metal interface of Figure 48a for aluminium (III) Haloflex on mild steel may thus be envisaged as existing in this interlayer.

The correlation between Al and Fe in the XPS images needs clarification in that the Al signal is detected into the metal side of the taper section i.e. it appears to exist beneath the prior metal substrate, although Al(III) was added into the polymer aqueous phase. The possibility of the smearing of polymer across the taper section onto the metal surface by the mill can be
discounted by the clear definition of polymer/interlayer boundary by the C1s image at 291 eV. On the contrary, the observed machining grooves which continue into the polymer coating suggest that smearing of polymer may have partially covered the interlayer but has left the metal substrate 'clean'. We can, therefore, suggest that the milling can easily produce a taper section in the brittle polymer (well below Tg), but on encountering the considerably harder and ductile metal substrate at a low grazing angle tends to deflect the coupon away from the mill. This effectively produces a taper section in the polymer and oxide and a flat metal side of the polymer/metal interface. The association of Fe and Al can, therefore, be attributed to be that existing at the metal interface and not beneath the surface.

The ESCASCOPE investigation has provided a valuable and clear confirmation of various proposed aspects of the interlayers formed between Haloflex and mild steel. The correlation of results from the different analyses and conclusions drawn are discussed in the next chapter together with a more mechanistic evaluation of Haloflex/steel interlayer formation.
DISCUSSION ON THE HALOFLEX COATING INTERACTIONS WITH AN IRON SUBSTRATE

The experimental Chapters 3-6 have individually attempted to characterise the formation and nature of the Haloflex coating and iron substrate interactions by a number of spectroscopic techniques. By combining the observations from these investigations it is possible to develop a mechanistic evaluation of substrate corrosion and subsequent anti-corrosive interlayer formation. The analyses of these chapters will, therefore, be reassessed in order to identify the basis for the interaction model.

The analysis of Chapter 3 identified an interfacial oxide film produced by the action of Haloflex binder on evaporated iron. Since the conversion of a binder to a paint coating effectively involves further additions of inert pigment (e.g. TiO$_2$, BaS$_2$ etc.) the properties of the binder and paint may be regarded as similar in terms of reactive species available. Hence, the interfacial oxide formed may be regarded as similar to that formed beneath a Haloflex paint. This oxide, identified as containing green rust I and $\alpha$-FeOOH is, therefore, the oxide film formed by the application and drying of Haloflex on an iron substrate. Thus, green rust I is present on the iron substrate prior to any subsequent immersion in oxidising electrolyte such as 3% NaCl.

This presence must be viewed in the light of A.C. impedance spectra obtained for Haloflex in 3% NaCl by Padget and Moreland (18) where a 9 day period is indicated as the time required for
formation of a protective interfacial layer. We have previously intimated that green rust I forms a protective interfacial anion exchange compound and attributed the enhancement of corrosion protection displayed by Haloflex paints to formation of this layer. However, there is an apparent contradiction in this respect, in that we have stated that green rust I exists prior to immersion in electrolyte and further proposed that the protective layer is formed after a 9 day period. We must, therefore, assume that the green rust interfacial layer formed on application of Haloflex is not continuous over the entire substrate.

On this assumption of initial partial coverage of the substrate with green rust I, we can attempt to model the formation of a complete protective film for the Haloflex/iron system when immersed in 3% NaCl solution. The test of the validity of this model can thus be assessed by comparison with the 9 day period associated with protective layer formation.

7.1. A Model for the Interfacial Oxide Formation Observed Beneath Haloflex Coatings

The diffusion of species through the Haloflex coating on immersion in 3% NaCl is shown schematically as Figure 104. To explain the formation of protective films, which we identify as a green rust type compound, several assumptions must initially be made.

i) Green rust is present at the interface as a consequence of application of Haloflex but is not a continuous protective film.
Figure 104  Haloflex coating in NaCl soln.
ii) The oxidation of iron to form green rust occurs via the mechanism proposed by Misawa et al. (41) in which a green complex is formed by the following reactions after Goto et al. (101)

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O} & \rightarrow \text{FeOH}^+ + \text{H}^+ \\
\text{O}_2 + \text{OH}^- & \rightarrow \text{O}_2\text{OH}^- \\
\text{FeOH}^+ + \text{O}_2\text{OH}^- & \rightarrow \text{green complex}
\end{align*}
\]

leading to hydrolysis of the FeOH\(^+\) ion

In the presence of suitable anions i.e. Cl\(^-\), the green complex is precipitated as green rust I.

iii) The diffusion of \(\text{O}_2\) to the reaction site (interface) will be the rate controlling step in the reaction process (i.e. Diffusion (\(\text{H}_2\text{O}\)) \gg Diffusion (\(\text{O}_2\)) from initial concentration considerations).

Therefore, assuming Fickian diffusion, the molar flux of oxygen, \(J\), through the coating to the interface will be given by:

\[
J = -D \frac{\delta c}{\delta x}
\]

where \(D\) = diffusion coefficient for oxygen in Haloflex

\[\approx 1 \times 10^{-6}\text{cm}^2\text{sec}^{-1}\]

\(\frac{\delta c}{\delta x}\) = concentration gradient

\[= \text{Conc. O in surface layer (C_{os})} - \text{conc. O at interface (C_{oi})}\]

coating thickness

\[x = 100\mu\text{m}\]

\(\text{C}_{oi}:\) As the diffusion of \(\text{O}_2\) is the rate controlling step we can assume that the concentration of \(\text{O}_2\) at the interface will be zero i.e. \(\text{O}_2\) is immediately consumed.

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To calculate Cos:

Considering a 1cm\(^2\) section of coating surface
the uptake of \(O_2\) into water is reported to be 3% by volume at 20\(^\circ\)C (102)
therefore, as 1 mole of \(O_2\) occupies \~25dm\(^{-3}\) at 20\(^\circ\)C, the number of
moles of \(O_2\) at 1cm\(^3\) of coating surface
is \(\frac{1}{25000} \times 0.03 = 1.2 \times 10^{-6}\) moles

However, water uptake into the surface of the coating is, for most
polymers, ca. 1% (104)
i.e. no. of moles of \(O_2\) in surface layer
\[= 1.2 \times 10^{-6} \times 0.01\]
\[= 1.2 \times 10^{-8}\) moles

therefore, in \(J = -D \frac{\delta c}{\delta x}\)
\[J = -1 \times 10^{-6} \times \frac{1.2 \times 10^{-8} - 0}{0.01}\]
\[= 1.2 \times 10^{-12}\) moles.sec\(^{-1}\)

Knowing the flux of \(O_2\), we must now consider the number of moles
of Fe that must be oxidised to form a green rust.

Padget and Moreland (18) measured iron pick-up in Haloflex
coated Q-panels immersed in 3% NaCl solution. They noted that
metal loss became significant after approximately 14 days and
corresponded to a 0.13\(\mu\)m thickness loss of the panels.
From these figures we can deduce that if we consider a 1cm$^2$ area of substrate surface the no. of moles of iron dissolved

\[ \text{volume of iron dissolved} \times \frac{\text{density}}{\text{molar mass}} \]

\[ \rho \text{ iron } = 7.6 \text{gcm}^{-3}, \quad M \text{ iron } = 56 \]

\[ = 0.13 \times 10^{-4} \times \frac{7.6}{56} \]

\[ = 1.76 \times 10^{-6} \text{ moles} \]

but from Misawa (41) the ratio of Fe(II)/Fe(III) in green rust I is ~1:1. We can, therefore, assume that from the more rapid diffusion of H$_2$O the iron dissolved will be in the divalent form FeOH$^+$ from the reaction

\[ \text{Fe} + \text{H}_2\text{O} = \text{FeOH}^+ + \text{H}^+ \]

If only 50% of the iron exists in trivalent form we need only oxidise

\[ 1.76 \times 10^{-6} \times 0.5 \]

\[ = 8.8 \times 10^{-7} \text{ moles} \]

Hence, if the molar flux (per second) of O$_2$ is $1.2 \times 10^{-12}$, the time for 50% oxidation of Fe(II) $\Rightarrow$ Fe(III) will be

\[ \frac{8.8 \times 10^{-7}}{1.2 \times 10^{-12}} \]

\[ = 7.33 \times 10^5 \text{ seconds} \]

\[ = 8.5 \text{ days} \]

This result of 8.5 days provides excellent agreement between
this theoretical argument and the experimental results of Padget and Moreland (18), hence the model must be regarded as being essentially valid.

The interpretation of initial incomplete green rust coverage on the metal substrate may be explained by reference to Figure 1 of Chapter 1, where adjacent anodic and cathodic sites are evoked by initial acidity and dissolved O₂ in the paint aqueous phase to produce Fe²⁺ and OH⁻ respectively. As the divalent Fe²⁺ is conveyed into the area of the cathode by diffusion etc. it may be hydrolysed (by reaction 3) to produce the trivalent Fe³⁺ and hence produce a green rust - Fe(II)/Fe(III) oxide. This protective oxide will, by polarisation of the cathode reaction, remain cathodic to neighbouring areas, which will actively corrode until initial acidity and dissolved O₂ are exhausted and complete polarisation of the corrosion reaction occurs. The remaining substrate would thus have green rust coverage only in prior cathodic sites.

Having established the mechanism of protective layer formation, we can consider how the addition of soluble ionic pigment may affect this process.

7.2. Modification of Interlayers by Ionic Additions

The requirement for oxidation of the divalent FeOH⁺ by hydrolysis to produce a trivalent species and hence green rust, could be alleviated by the availability of a suitable trivalent
species in the vicinity of the reaction site. Aluminium (III) would seem a suitable choice of ionic addition because of its known formation of a pyroaurite with iron, and could therefore provide two distinct mechanisms of interlayer formation involving iron.

Firstly, aluminium (III) may be incorporated into the oxide formed on drying. Alternatively after drying and ingress of H₂O, aluminium (III) taken into solution would again present a trivalent species without the need for O₂ diffusion and subsequent hydrolysis of FeOH⁺. The kinetics of Al(III) protection, therefore, require investigation after a suitable paint formulation can be designed to incorporate a soluble Al(III) pigment, in order to assess the validity of this argument.

However, the association of Fe and Al has clearly been demonstrated by a number of methods. TEM has demonstrated the morphology of the diffuse interface into the polymer indicating at various points the presence of Al by EDX determination. Electron diffraction has indicated that this interlayer is, at least partially, comprised of a pyroaurite type structure again confirming our hypothesis of protective interfacial film formation. Finally the ESCASCOPE investigation could be interpreted in association with the TEM morphology information, to identify an Al/Fe oxide interlayer with enriched chlorine existing as the diffuse interface growing into the coating and an Al/Fe interlayer on the metal surface. The aluminium (III) enriched interlayer was thus achieved and displayed similar properties to the green rust formation in 'normal' Haloflex paints when tested
electrochemically by A.C. impedance spectroscopy albeit in a poor paint film.

The addition of magnesium (II) into the Haloflex coating was a partly speculative attempt to obtain a totally novel method of paint film protection. Investigation by TEM had demonstrated that the initial acidic etching of a metal substrate had deposited iron at the polymer/air surface by convection. It was, therefore, realised that this iron which should readily be oxidised to Fe(III) could be provided with an intimately mixed divalent ion, Mg(II).

A simple experiment was performed to illustrate our proposal. A Q-panel was coated with a normal Haloflex paint with a single coat of wet thickness ~100μm. Immediately after application, two pipettes were used to place a small amount of potassium hexacyanoferrate (III) and potassium hexacyanoferrate (II) on the coating surface at intervals of 30 secs. traversing the length of the Q-panel. Potassium hexacyanoferrate (III) is an indicator for Fe^{2+} ions - turning a prussian blue colour, and likewise potassium hexacyanoferrate (II) gives a blue colouration in the presence of Fe^{3+} ions.

Over a series of tests it was established that divalent ions were evident on the polymer surface after 3-6 minutes. However, the trivalent ions were not observed until considerably later i.e. 2-3 hours, by which time the Haloflex coating was touch dry (although the latex is by no means fully coalesced). It can then be assumed that the oxidation of Fe(II) → Fe(III) occurs once the
influence of the acidic aqueous phase is removed, although water loss (evaporation) will still be continuing at this stage at a diminished rate.

TEM, SEM and XPS have all demonstrated the formation of a surface layer containing magnesium and iron in magnesium (II) solution pigmented Haloflex. It must, therefore, be assumed that ionic mobility in this diminished drying rate is still sufficient to allow Mg(II) to diffuse the Fe rich surface layer to form a protective layer; the nature of which has been ably demonstrated by A.C. impedance spectroscopy.

The formation and nature of interfacial layers formed in Haloflex on mild steel can, therefore, be stated in a series of conclusions. These will be presented as Chapter 8.
The following conclusions can be drawn from the work presented in this thesis.

(i) The action of the acidic water-based vinyl acrylic copolymer (Haloflex) on application to mild steel substrates is to produce rapid etching of the surface oxide/hydroxide followed by anodic dissolution of iron at the substrate surface to provide $\text{Fe}^{2+}$ ions.

(ii) The $\text{Fe}^{2+}$ ions initially produced at the substrate surface are carried by convection currents in the evaporating aqueous phase and deposited at the coating surface where flocculation of latex particles is induced by ionic interaction with the latex surfactant.

(iii) Flocculation of the outer coating layer diminishes the convection currents in the aqueous phase and leaves a coating surface layer rich in Fe.

(iv) Partial oxidation of the $\text{Fe}^{2+}$ ions produced at the polymer/metal interface causes an interfacial oxide to be produced. This interlayer is found to be enriched in chlorine bound as inorganic species and comprises, in part, of a mixed valence Fe(II)/Fe(III) oxide - green rust I. Green rust I is found not initially to exist as a continuous film over the substrate.
(v) Determination of the Fe(II)/Fe(III) ratio of dissolved iron species through the polymer coating indicates that the polymer/metal interface region departs from the bulk pH of the applied coating in that alkalinity is produced by the cathodic reduction of oxygen to form OH\(^{-}\) ions. This pH departure is necessary to produce the environment for green rust formation.

(vi) Subsequent exposure of Haloflex coated mild steel to an aqueous environment enables further partial oxidation of divalent Fe\(^{2+}\) species to produce a continuous protective interlayer of green rust.

(vii) Additions of soluble pigment containing Al(III) and Mg(II) can modify the oxidation behaviour of dissolved Fe species. Al(III) can combine with divalent Fe\(^{2+}\) at the polymer/metal interface to produce a pyroaurite-type interfacial oxide and also a diffuse layer in the coating intimately mixed with latex polymer. Mg(II) can combine with trivalent Fe\(^{3+}\) at the polymer/air interface to produce a coating surface film.

(viii) Soluble pigment modified interfacial layers have been demonstrated to provide enhanced anti-corrosive behaviour in Haloflex coatings. Al(III) modified coatings have shown behaviour similar to 'normal' Haloflex coating despite the actual latex coating properties deteriorating due to excessive pigment solution addition. Mg(II) modified coatings display exceptional anti-corrosive behaviour when immersed in 3% NaCl solution.
The potential to utilise the family of pyroaurite compounds has clearly been demonstrated in organic coatings. Future work is needed to develop latex systems which can incorporate ionic species in the aqueous phase without loss of surfactant properties. Such paints could then be tested by conventional industry standards to fully evaluate potential as high performance anti-corrosive coatings.
APPENDIX I

Formulation of Haloflex paint used in this study

<table>
<thead>
<tr>
<th>Ingredient</th>
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<tbody>
<tr>
<td>Haloflex 202</td>
<td>59.2</td>
</tr>
<tr>
<td>Synperonic PE 39/70 (30''')</td>
<td>3.1</td>
</tr>
<tr>
<td>Barytes</td>
<td>23.1</td>
</tr>
<tr>
<td>Titanium dioxide</td>
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<tr>
<td>Bevaloid 642</td>
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<tr>
<td>Methocel J12 M5</td>
<td>0.2</td>
</tr>
<tr>
<td>Butyl ethoxol</td>
<td>2.0</td>
</tr>
<tr>
<td>Water</td>
<td>10.7</td>
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</table>

20% pigment volume concentration
pH: 5-6
volume solids: 44%
viscosity: 2 poise (180s⁻¹)

Notes on ingredients

a) Haloflex 202 (function:- binder) 60% solids pH 1-2 particle size -0.2mm particle charge - anionic - low permeability makes it suitable as a primer.

b) Synperonic PE 39/70 (function:- stabiliser/dispersant) a non-ionic surfactant with high ethylene oxide content. It is a block copolymer of propylene oxide and ethylene oxide, which enhances film coalescence, pigment dispersion and storage stability.
c) Bevaloid 642 - (defoamer)
e) Butyl ethoxol (coalescing solvent). The coalescing solvent reduced the minimum film forming temperature of the paint and allows it to coalesce over a wider range of application temperatures.
ACCELERATING VOLTAGE 100kV \rightarrow \lambda = 0.0037\text{nm}

CAMERA LENGTH \( L = 2710\text{mm} \)

MEASURED DISC SPACING \( R = 13.4\text{mm} \)

FROM BRAGGS' LAW I.E.

\[
D = \frac{\lambda \cdot L}{R}
\]

\[
D = \frac{0.0037 \cdot 2710}{13.4} \text{ nm}
\]

\approx 0.75\text{nm}, \ 7.5\text{Å}

DIFFRACTED DISC CORRESPONDS TO AN INTERPLANAR D-SPACING OF BETWEEN 7 AND 8 ANGSTROMS - INDICATIVE OF A PYROAURITE-TYPE STRUCTURE.

APPENDIX 2
Schematic illustration of electron diffraction pattern d spacing determination.
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<th>Region: FE2P</th>
<th>TECHNIQUE: XPS</th>
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<th>SPECTRUM PARAMETERS</th>
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<td>Acquisition (S):</td>
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File label: HALO ON STEEL
MILL -15 SAXPS
METAL REGION

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<th>Region: FE2P</th>
<th>TECHNIQUE: XPS</th>
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File label: HALO MG SAME AS MILL
APP A1 POLY SURFACE
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